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(54) TONER AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a toner which has excellent spectral characteristics such as transparency required to reproduce the clear color tone of a color image when applied to a color toner and is less liable to fog, and with which printing density is increased and excellent durability of printing is realized, and to provide a method for manufacturing the same.

SOLUTION: The toner comprises a bonding resin, a colorant, a positive charge controlling resin, and a negative charge controlling resin, wherein the positive charge controlling resin is a polyester resin obtained by polycondensing a polycarboxylic acid compound (A1) containing an amino group or its salt and/or a polyol (A2) containing an amino group or its salt, and the negative charge controlling resin is a polyester resin obtained by polycondensing a polycarboxylic acid compound (J1) containing a sulfonic acid group or its salt and/or a polyol (J2) containing a sulfonic acid group or its salt.

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CLAIMS

[Claim(s)]

[Claim 1]It is polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) which contains binding resin, colorant, right electrification control resin, and negative electrification control resin, and in which this right electrification control resin contains an amino group or its salt and/or an amino group, or its salt, A toner which is polyester resin which carries out the polycondensation of the polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) in which this negative electrification control resin contains a sulfonic group or its salt and/or a sulfonic group, or its salt.

[Claim 2]The toner according to claim 1 whose number of color particles with a major axis of 0.2 micrometers or more observed in an area of 100 micrometers x 100 micrometers of a toner which carried out heat melting and was made into 20 micrometers of thickness is 50 or less pieces.

[Claim 3]A manufacturing method of a toner characterized by comprising the following.
Right electrification control resin 100 weight section which consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing an amino group or its salt and/or an amino group, or its salt.

Ten to colorant 200 weight section.

Zero to organic solvent 100 weight section which may dissolve this right electrification control resin is mixed, Negative electrification control resin 100 weight section which consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a process of obtaining a right electrification control resin composition and a sulfonic group, or its salt and/or a sulfonic group, or its salt.

A process of mixing ten to colorant 200 weight section, and zero to organic solvent 100 weight section which may dissolve this negative electrification control resin, and obtaining a negative electrification control resin composition.

[Claim 4]A manufacturing method of the toner according to claim 3 characterized by comprising the following.

Said 0.1 to right electrification control resin composition 20 weight section.

Said 0.1 to negative electrification control resin composition 20 weight section.

Polymerization nature monomer 100 weight section is mixed, a polymerization nature monomer composition is obtained, and this constituent is polymerized in a drainage system carrier fluid body.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to a toner and a manufacturing method for the same. In detail, it is related with a clear color tone, stable electrification, a toner that has the outstanding transfer nature, and a manufacturing method for the same irrespective of an one-ingredient method and a two-ingredient method.

[0002]

[Description of the Prior Art]In recent years, the full color electrophotography device, especially the digitized full color electrophotography device attract attention, and it is being widely developed by the commercial scene with expansion of automation. As a toner for electro photography (it may only be hereafter called a "toner".) used for an electrophotography device, The particles which add and knead colorant, a charge controlling agent, etc. to binding resin, and are subsequently mainly manufactured by grinding and what is called pulverizing method classified further (pulverizing method particles), Or the particles (the polymerizing method particles) manufactured by polymerizing by methods, such as suspension polymerization, an emulsion polymerization, and a distributed polymerization, and making mixtures, such as a polymerization nature monomer, colorant, and a charge controlling agent, meet if needed are mainly used. The toners used for it differ and it is classified into the negative triboelectric charging toner and the positive triboelectric charging toner according to the electrifying system of a photo conductor.

[0003]Colorization progresses also in a xerography these days and the color toner corresponding to a color image forming device is called for. Equipping a color image forming device with two or more image formation parts, forming the toner image from which a color differs by each image formation part, respectively, and color-printing by putting the color toner image of yellow, magenta, cyanogen, black, etc. on the same recording medium one by one, and transferring it is known. Even though it uses any, such as pulverized toner and polymerization toner, the following [use / as color toner] is demanded.

[0004](1) Transparency of a toner is high in order to carry out a multicolor pile.

(2) In order to make a color reproduce, a spectrum reflection property be excellent.

(3) Control electrification of a toner positive or negative precisely.

(4) Low temperature fixation be possible.

(5) Manufacture of color toner be easy.

[0005]Various examination is performed in order to meet these demands. For example, in JP,61-149969,A. The toner composition which grinds the paints processed with the additive agent for electrification strengthening which mixed and prepared additive agents for electrification strengthening, such as a homogeneous polymer of an amine content monomer, and paints by the roll mill among halogenated hydrocarbon, such as chloroform, after melting mixing with a resin particle is indicated. In JP,62-119549,A, binding resin is dissolved in a solvent, colorant and a charge controlling agent are added into this solution, a solvent is removed with a freeze drying method after stirring mixing, and the toner production method which carries out grinding classification of the toner subsequently obtained is indicated. In JP,03-155568,A, binding resin

and at least one of a color and the paints. The mix of the organic solvent is carried out, the masterbatch of a color or paints is manufactured, and the manufacturing method of the toner which accepts binding resin and necessity further, kneads by mixing other additive agents and carries out grinding classification of this masterbatch is indicated. To JP,4-242752,A, paints are heated in binding resin, Melting and kneading of the pitch powder type paints produced by carrying out application-of-pressure kneading are carried out with binding resin, and the manufacturing method of the color toner to distribute and the color toner which the number rate of a paints particle of 0.3 micrometers or more is distributing at 0.1% or less with the circular nominal diameter which exists in binding resin are indicated.

[0006]However, it is fairly difficult to satisfy the demand of the versatility of said color toner simultaneously also by these methods. Especially the thing for which it has the stable electrostatic property, and it excels in transparency and the good color toner of a spectrum reflection property is manufactured was difficult.

[0007]

[Problem(s) to be Solved by the Invention]In electro photography, the purpose of this invention can acquire a clear picture and there is in providing a toner with which electrostatic property does not change even if placed under different environment, and a manufacturing method for the same. When it applies to especially color toner, it excels in the spectral characteristics, such as transparency required for reappearance of the clear color tone of a color picture, and there is little fogging, and printing density can be made high, and also it is in providing a toner excellent also in durable printing nature, and a manufacturing method for the same. As a result of repeating research wholeheartedly to achieve the above objects, this invention person is using right electrification control resin and negative electrification control resin which consist of specific polyester resin, finds out that said purpose can be attained, and came to complete this invention.

[0008]

[Means for Solving the Problem]According to this invention, (1) binding resin, colorant, right electrification control resin, and negative electrification control resin are contained in this way. It is polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) in which this right electrification control resin contains an amino group or its salt and/or an amino group, or its salt, A toner which is polyester resin which carries out the polycondensation of the polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) in which this negative electrification control resin contains a sulfonic group or its salt and/or a sulfonic group, or its salt, (2) Right electrification control resin 100 weight section which consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing an amino group or its salt and/or an amino group, or its salt, A process of mixing ten to colorant 200 weight section, and zero to organic solvent 100 weight section which may dissolve this right electrification control resin, and obtaining a right electrification control resin composition, And negative electrification control resin 100 weight section which consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group or its salt and/or a sulfonic group, or its salt and ten to colorant 200 weight section, Zero to organic solvent 100 weight section which may dissolve this negative electrification control resin is mixed, and manufacturing method ** of a toner having the process of obtaining a negative electrification control resin composition is provided.

[0009]

[Embodiment of the Invention]The toner of this invention contains binding resin, colorant, right electrification control resin, and negative electrification control resin at least. The right electrification control resin contained in the toner of this invention consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing the polyvalent-carboxylic-acid compound (A1) containing an amino group or its salt and/or an amino group, or its salt. An amino group or its salt is not contained in polyhydric alcohol (A2) containing the polyvalent-carboxylic-acid compound (A1) containing the amino group mentioned later or its salt

and/or an amino group, or its salt, and the other polyvalent-carboxylic-acid compounds or polyhydric alcohol which can carry out copolycondensation.

[0010]As a polyvalent-carboxylic-acid compound (A1) containing the amino group which constitutes polyester resin as right electrification control resin, or its salt, Aminoterephthalic acid, 5-aminoisophthalic acid, 5-aminoisophthalic acid methyl ester, 4-aminophthalic acid, 4-aminophthalic acid anhydride, 4-aminonaphthalene 2,7-dicarboxylic acid, 5 - [4-aminophenoxy] Aromatic polyvalent carboxylic acid, such as isophthalic acid; 5-amino hexahydro isophthalic acid, 5-amino hexahydro isophthalic acid methyl ester, 4-amino hexahydrophthalic acid, 4-amino hexahydrophthalic anhydride; alicyclic-polycarboxylic-acid [, such as 5-amino tetrahydro isophthalic acid, 5-amino tetrahydro isophthalic acid methyl ester, 4-amino tetrahydrophthalic acid, and 4-amino tetrahydrophthalic anhydride,]; etc. are mentioned. As polyhydric alcohol (A2) containing an amino group or its salt, Chain aliphatic-polyhydric-alcohol; 2-amino-4-hydroxymethylbenzyl alcohol, such as 2-amino-2-methyl-1,3-propanediol and diethanolamine, 2-amino-3-hydroxymethylbenzyl alcohol, 4-amino-2-hydroxymethylbenzyl alcohol, Aromatic polyhydric alcohol, such as 5-amino-3-hydroxymethylbenzyl alcohol; alicycle fellows polyhydric alcohol; such as 2,4-bis(hydroxyethyl)-1-aminocyclohexane, and those ammonium salt are mentioned.

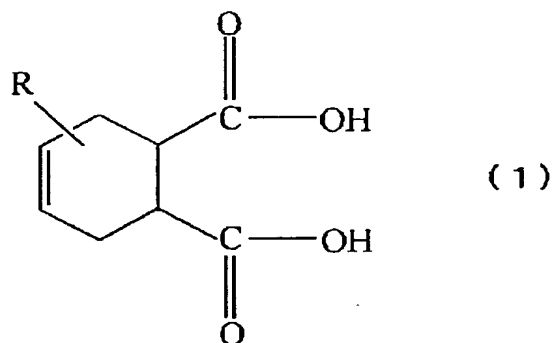
[0011]The polyester resin which has ammonium salt, Copolycondensation of the polyhydric alcohol (A2) which has the polyvalent-carboxylic-acid compound (A1) and/or ammonium salt which have the ammonium salt like the above may be carried out, and, After carrying out copolycondensation of the polyhydric alcohol (A2) which has the polyvalent-carboxylic-acid compound (A1) and/or amino group which have an amino group, what was ammonium-salt-ized may be used. In polyester resin as right electrification control resin contained in the toner of this invention, The quantity of polyhydric alcohol (A2) containing the polyvalent-carboxylic-acid compound (A1) containing an amino group or its salt and/or an amino group, or its salt, the total monomer (sum total of all the carboxylic acid components and all the alcohol components) which constitutes polyester resin — usually — 0.2-30-mol % — it is 0.5-10-mol % preferably. By containing this polyvalent-carboxylic-acid compound (A1) and/or polyhydric alcohol (A2) as a polycondensation ingredient, the dispersibility of the paints in a toner can improve and the electrostatic property of a toner can be controlled.

[0012]As for polyester resin as right electrification control resin, it is preferred that copolycondensation of the cyclic divalent-carboxylic-acid compound (B) is carried out further. As a cyclic divalent-carboxylic-acid compound (B), an aromatic divalent-carboxylic-acid compound and an alicycle fellows divalent-carboxylic-acid compound are mentioned, and an alicycle fellows divalent-carboxylic-acid compound is preferred. As an aromatic divalent-carboxylic-acid compound, derivatives, such as 1,5-naphthalic acid, 2,6-naphthalic acid, diphenic acid, terephthalic acid, isophthalic acid, phthalic acid, these alkylation objects and these acid anhydrides, a halogenide, ester, and amide, are mentioned.

[0013]An alicycle fellows divalent-carboxylic-acid compound is a compound in which fat ring structure, two carboxyl groups, or a carboxylic acid derivative group exists in molecular structure. As fat ring structure, the thing of many rings, such as monocycle; norbornane rings, such as a cyclopentane ring, a cyclohexane ring, a cycloheptane ring, and a cyclohexene ring, and a norbornene ring, is mentioned. As a suitable alicycle fellows divalent-carboxylic-acid compound, a carboxyl group or a carboxylic acid derivative group (an amide group, an ester group, and an acid anhydride group.) The alicycle fellows divalent-carboxylic-acid compound which acid halide combines with each two carbon atom which constitutes alicycle; an alkyl group like the alicycle fellows divalent carboxylic acid expressed with the general formula (1) or (2) or those anhydrides has combined with alicycle as a substituent. [especially] As an alkyl group, a methyl group, an ethyl group, a propyl group, an isopropyl group, etc. are preferably mentioned to the thing of 1-8 carbon numbers, and a concrete target.

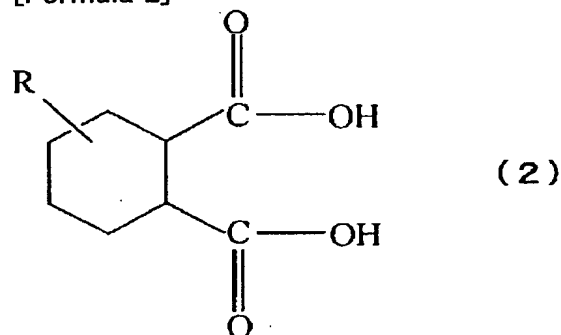
[0014]

[Formula 1]



[0015]

[Formula 2]



[0016]R in a formula (1) or (2) is an alkyl group.

[0017]An alicycle fellows divalent-carboxylic-acid compound preferably used for polyester resin as right electrification control resin makes a diene compound and; maleic anhydrides, such as butadiene, isoprene, piperylene, and a cyclopentadiene, react, and is obtained by hydrogenating if needed etc., for example. As an example of an alicycle fellows divalent-carboxylic-acid compound, Tetrahydro terephthalic acid, tetrahydro isophthalic acid, tetrahydrophthalic acid; Hexahydro terephthalic acid, Hexahydro isophthalic acid, hexahydrophthalic acid; 3-alkyl tetrahydro terephthalic acid, 4-alkyl tetrahydro terephthalic acid, 3-alkyl tetrahydro isophthalic acid, 4-alkyl tetrahydro isophthalic acid, 3-alkyl tetrahydrophthalic acid, 4-alkyl tetrahydrophthalic acid; 3-alkyl hexahydro terephthalic acid, 4-alkyl hexahydro terephthalic acid, 3-alkyl hexahydro isophthalic acid, 4-alkyl hexahydro isophthalic acid, 3-alkyl hexahydrophthalic acid, 4-alkyl hexahydrophthalic acid; 3,6- and methylene-tetrahydro terephthalic acid, 3,6- and methylene-tetrahydro isophthalic acid, 3,6-, methylene-tetrahydrophthalic acid; 3,6- and methylene-hexahydro terephthalic acid, 3,6- and methylene-hexahydro isophthalic acid, 3,6-, and methylene-hexahydrophthalic acid;

[0018]2-alkyl 3,6- and methylene-tetrahydro terephthalic acid, 3-alkyl 3,6- and methylene-tetrahydro terephthalic acid, 2-alkyl 3,6- and methylene-tetrahydro isophthalic acid, 3-alkyl 3,6- and methylene-tetrahydro isophthalic acid, 2-alkyl 3,6- and methylene-tetrahydrophthalic acid, and 3-alkyl 3,6-, methylene-tetrahydrophthalic acid; 2-alkyl 3,6-, and methylene-hexahydro terephthalic acid, 3-alkyl 3,6- and methylene-hexahydro terephthalic acid; 2-alkyl 3,6- and methylene-hexahydro isophthalic acid, 3-alkyl 3,6- and methylene-hexahydro isophthalic acid, and 2-alkyl 3,6- and methylene-hexahydrophthalic acid, and 3-alkyl 3,6- and methylene-hexahydrophthalic acid; are mentioned.

[0019]As an example of a derivative of an alicycle fellows divalent-carboxylic-acid compound, A tetrahydrophthalic anhydride, a hexahydrophthalic anhydride, 3-alkyl tetrahydrophthalic anhydride, Acid anhydrides, such as 3-alkyl hexahydrophthalic anhydride, 4-alkyl tetrahydrophthalic anhydride, and 4-alkyl hexahydrophthalic anhydride; a halogenide, ester, amide, etc. are mentioned. These are independent, respectively or can be used combining two or more sorts. Also in these, 3-alkyl tetrahydrophthalic acid, 3-alkyl hexahydrophthalic acid, Since a toner which is excellent in the dispersibility of colorant is obtained when the melting

characteristic becomes high and 4-alkyl tetrahydrophthalic acid, 4-alkyl hexahydrophthalic acid, and these anhydrides use this polyester resin for a toner, it is desirable. As for quantity of a cyclic divalent-carboxylic-acid compound (B), it is preferred especially that it is [80 – 100 mol] % usual [of all the polyvalent carboxylic acid components which constitute polyester resin], 70 – 100-mol%. If there are few these rates, sufficient preservability of a toner may not be acquired.

[0020]As carboxylic acid components which constitute polyester resin as right electrification control resin, copolycondensation of a chain divalent-carboxylic-acid compound (D) and the carboxylic acid compound (F) more than trivalent may be carried out if needed. As a chain divalent-carboxylic-acid compound (D) in which copolycondensation is possible, succinic acid, adipic acid, azelaic acid, sebacic acid, dodecane dicarboxylic acid, fumaric acid, maleic acid, itaconic acid, etc. are mentioned. As a polyvalent-carboxylic-acid compound (F) more than trivalent, trimellitic acid, pyromellitic acid, trimesic acid, etc. are mentioned. Less than 30 mol % of all the carboxylic acid components of a rate of a chain divalent-carboxylic-acid compound (D) is preferred. When this rate becomes large, glass transition temperature and melt viscosity become low, the blocking resistance of a toner may fall or hot offset may occur. Less than 5 mol % of all the carboxylic acid components of a rate of a polyvalent-carboxylic-acid compound (F) more than trivalent is preferred. Since weight average molecular weight of polyester resin will become high if this rate becomes large, melt viscosity of a toner may become high and the fixability of a toner may worsen.

[0021]As for polyester resin as right electrification control resin contained in a toner of this invention, it is preferred that copolycondensation of the cyclic dihydric alcohol (C) is carried out further. As cyclic dihydric alcohol (C), aromatic dihydric alcohol and alicycle fellows dihydric alcohol are mentioned, and alicycle fellows dihydric alcohol is preferred. As aromatic dihydric alcohol, PARAKI silylene glycol, meta key silylene glycol, An ethyleneoxide addition of Alt key silylene glycol and 1,4-phenyleneglycol, an ethyleneoxide addition of bisphenol A, a propylene oxide addition, etc. are mentioned. As alicycle fellows dihydric alcohol, it is 2,2-bis(4-hydroxycyclohexyl)-propane (.). Namely, hydrogenation bisphenol A, 1,4-bis(hydroxymethyl)cyclohexane, 1,3-bis(hydroxymethyl)cyclohexane, 1,2-bis(hydroxymethyl)cyclohexane, 2,2,4,4-tetramethyl 1,3-cyclohexanediol, An ethyleneoxide addition of 1,4-cyclohexanediol and hydrogenation bisphenol A and a propylene oxide addition, tricyclodecane diol, tricyclodecane dimethanol, dicyclohexyl 4,4'-diol, etc. are mentioned. Bis(hydroxycyclohexyl)-alkanes, such as hydrogenation bisphenol A, are [among these] preferred. Quantity of cyclic dihydric alcohol (C) is preferred in their being 2 – 60-mol% of all the polyhydric alcohol components which constitute polyester resin, and still more preferred in their being 3 – 50-mol %. If glass transition temperature and melt viscosity become low, blocking resistance may fall, or hot offset may occur, when there is too little quantity of cyclic dihydric alcohol (C), and quantity of alicycle fellows dihydric alcohol increases too much conversely, Melt viscosity may become high and fixability may fall.

[0022]As other alcohol components which constitute polyester resin as right electrification control resin, it is preferred that copolycondensation of the chain dihydric alcohol (E) is carried out further. Copolycondensation of the alcohol (G) more than trivalent may be carried out. As chain dihydric alcohol (E), ethylene glycol, a diethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol, polyethylene glycols, Straight-chain-shape aliphatic series glycols, such as polytetramethylene glycol; Propylene glycol, Branched-chain aliphatic series glycols, such as dipropylene glycol, polypropylene glycol, neopentyl glycol, 2,2,4-trimethyl 1,3-pentanediol, and 2-ethyl-2-butyl-1,3-propanediol, etc. are mentioned. In these, straight-chain-shape aliphatic series glycol is preferred, and especially ethylene glycol is preferred also in it. Quantity of chain dihydric alcohol (E) is preferred in their being 40 – 98-mol% of all the polyhydric alcohol components which constitute polyester resin, and still more preferred in their being 50 – 97-mol %. When melt viscosity may become high, fixability may fall, when there is too little quantity of chain dihydric alcohol (E), and quantity of chain dihydric alcohol increases too much conversely, glass transition temperature and melt viscosity become low, blocking resistance may fall or hot offset may occur. As alcohol (G) more than trivalent, trimethylolpropane, glycerin, pentaerythritol, dipentaerythritol, trimethylolethane, cyclohexane

triol, tris(hydroxymethyl) cyclohexane, etc. are mentioned. Less than 5 mol % of all the alcohol components of a rate of alcohol (G) more than trivalent is preferred. Since weight average molecular weight of polyester resin will become high if this rate becomes large, melt viscosity of a toner may become high and the fixability of a toner may worsen.

[0023]A molecular weight of polyester resin as right electrification control resin contained in a toner of this invention, When it measures with gel permeation chromatography (GPC), by polystyrene conversion. a number average molecular weight — 1,500–20,000 — it is 2,000–10,000 preferably — weight average molecular weight — desirable — 5,000–300,000 — it is 7,000–100,000 preferably. When a molecular weight is in this range, a toner excellent in low temperature fixability and hot offset tolerance can be obtained. When a number average molecular weight and weight average molecular weight are smaller than a mentioned range, cohesive force of resin may decline, preservability may get worse, when conversely large, productivity may fall and the fixability of a toner may get worse. 40–90 °C of glass transition temperature of electrification control resin is 50–80 °C especially preferably. The preservability of a toner will be improved if glass transition temperature is a mentioned range.

[0024]A hydroxyl value is usually 1 – 100 mgKOH/g, and polyester resin as right electrification control resin is a thing of 5 – 80 mgKOH/g preferably. When a hydroxyl value is small, fixability may worsen, big unevenness may arise on the surface of a picture, and smooth nature may fall. Conversely, when large, hot offset generating temperature becomes low, hydrophilic nature becomes high further, and it is in a tendency for electrification quantity to change with environmental variations easily. As for electrification control resin, in order to lessen influence of moisture in a high-humidity/temperature environment, it is preferred to lessen an aromatic ring more.

[0025]Polyester resin as right electrification control resin contained in a toner of this invention can be manufactured by a publicly known method, i.e., a polycondensation method. A total of a hydroxyl value of the inside of a total monomer which totaled a polyvalent carboxylic acid component and a polyhydric alcohol component in carrying out the polycondensation of a polyvalent carboxylic acid component and the polyhydric alcohol component, and an alcoholic reactivity group [X] A total of acid value of said carboxylic acid sexual response nature group [Y] Since also performing a twist on conditions which do not become small can make a molecular weight of polyester high and it can make a hydroxyl value high, it is preferred. A total of a hydroxyl value of an alcoholic reactivity group [X] A total of acid value of a carboxylic acid sexual response nature group [Y] Rate[X]/1.00 or more equivalent ratio of [Y] is preferred, 1.01–1.5 are more preferred, and especially the range of 1.03–1.3 is preferred. The alcoholic reactivity group refers to an alcoholic functional group in which an ester bond is made to form here, and hydroxyl etc. are usually mentioned. The carboxylic acid sexual response nature group refers to a functional group of carboxylic acid nature in which an ester bond is made to form, and a carboxyl group or a carboxylic acid derivative group is usually mentioned.

[0026]As for a polycondensation reaction, it is preferred that it is carried out at 150–280 °C, and reaction temperature of 100–300 °C carries out especially under existence of inactive gas preferably for example. An organic solvent of nonaqueous solubility which carries out azeotropy to water, such as toluene and xylene, may be used if needed. A polycondensation reaction may be performed under decompression (usually 0.1 – 500mmHg, preferably 0.5 – 200mmHg, more preferably 1 – 50mmHg). An esterification catalyst is usually used for this polycondensation reaction. As an esterification catalyst, for example Para toluenesulfonic acid, sulfuric acid, Broensted acid, such as phosphoric acid; Calcium acetate, zinc acetate, manganese acetate, zinc stearate; — acetylacetonato [of iron or zinc]; — metal alkoxide; — alkyl tin oxide. Organic metallic compounds, such as dialkyl tin oxide and an organic titanium compound : Tin oxide, Metallic oxides, such as antimony oxide, titanium oxide, and vanadium oxide: Titanium alkoxide, heteropoly acid, or iron acetylacetonato is preferred at a point which can carry out polymers quantification of the polyester obtained by mentioning heteropoly acid etc.

[0027]In order to obtain polyester resin as right electrification control resin contained in a toner of this invention, the above-mentioned carboxylic acid compound and alcohol may be prepared and put in block, and may be made to react by desired composition ratio, and a following method

can also be used in order to adjust a molecular weight. Namely, a cyclic divalent-carboxylic-acid compound (B) and cyclic dihydric alcohol (C) preferably, Carry out the polycondensation of a cyclic divalent-carboxylic-acid compound (B), cyclic dihydric alcohol (C) and a chain divalent-carboxylic-acid compound (D), and/or the chain dihydric alcohol (E), obtain a precursor, and it ranks second, The polycondensation of polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing this precursor, an amino group, or its salt and/or an amino group, or its salt and a polyvalent-carboxylic-acid compound (H), and/or polyhydric alcohol (I) is carried out.

[0028]a time of measuring a precursor with gel permeation chromatography (GPC) — polystyrene conversion — the number average molecular weight — 1,500–5,000 — it is 2,000–4,000 preferably. The dispersibility of resin becomes high when a molecular weight is in this range. Not less than 40 ** of glass transition temperature of a precursor is 50–80 ** especially preferably preferably. The preservability of a toner will be improved if glass transition temperature is not less than 40 **.

[0029]A polyvalent-carboxylic-acid compound (H) which carries out copolycondensation to polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing a precursor and an amino group, or its salt and/or an amino group, or its salt, Especially, it is not restricted but an aromatic divalent-carboxylic-acid compound which was mentioned above and a cyclic divalent-carboxylic-acid compound (B) like an alicycle fellows dicarboxylic acid compound, a chain divalent-carboxylic-acid compound (D), a carboxylic acid compound (F) more than trivalent, etc. can be mentioned. A cyclic divalent-carboxylic-acid compound which a carboxyl group or a carboxylic acid derivative group combined with each two carbon atom like terephthalic acid, tetrahydro terephthalic acid, and hexahydro terephthalic acid which constitutes a ring, and which does not adjoin each other also in these is preferred. Polyhydric alcohol (I) which carries out copolycondensation to polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing a precursor and an amino group, or its salt and/or an amino group, or its salt, Especially, it is not restricted but cyclic dihydric alcohol (C) like aromatic dihydric alcohol which was mentioned above, or alicycle fellows dihydric alcohol, chain dihydric alcohol (E), alcohol (G) more than trivalent, etc. can be mentioned. The total quantity of a polyvalent-carboxylic-acid compound (H) used for copolycondensation with a precursor or polyhydric alcohol (I) is 20 – 40 weight section especially preferably ten to 50 weight section preferably to precursor 100 weight section. When quantity of this polyvalent-carboxylic-acid compound or polyhydric alcohol is in a mentioned range, since polymers quantification can be carried out without spoiling the melting characteristic, it is desirable.

[0030]Negative electrification control resin contained in a toner of this invention consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group or its salt and/or a sulfonic group, or its salt. This negative electrification control resin polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing an amino group which constitutes right electrification control resin mentioned above, or its salt and/or an amino group, or its salt, It can obtain by transposing to polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group or its salt and/or a sulfonic group, or its salt, and carrying out a polycondensation to it. Therefore, a cyclic divalent-carboxylic-acid compound (B) which can carry out copolycondensation, What was mentioned above can be used for a carboxylic acid compound (F) more than cyclic dihydric alcohol (C), a chain divalent-carboxylic-acid compound (D), chain dihydric alcohol (E), and trivalent, and alcohol (G) more than trivalent. An above-mentioned method can also make the manufacturing method the same.

[0031]As a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group which constitutes polyester resin as negative electrification control resin, or its salt, Sulfoterephthalic acid, 5-sulfoisophtharate, 5-sulfoisophtharate methyl ester, 4-sulfophthalic acid, 4-sulfophthalic acid anhydride, 4-sulfonaphthalene-2,7-dicarboxylic acid, 5 – [4-sulfophenoxy] Isophthalic acid; 5-sulfo hexahydro isophthalic acid, 5-sulfo hexahydro isophthalic acid methyl ester, Aromatic multivalent sulfonic acid;5-sulfo tetrahydro isophthalic acid, such as 4-sulfo hexahydrophthalic acid and 4-sulfo hexahydrophthalic anhydride, Alicycle fellows multivalent sulfonic acid [, such as

5-sulfo tetrahydro isophthalic acid methyl ester, 4-sulfo tetrahydrophthalic acid, and 4-sulfo tetrahydrophthalic anhydride,]; those salts, etc. are mentioned. As a sulfonate, salts, such as ammonium, Li, Na, K, Mg, Ca, Cu, and Fe, are mentioned. In particular, K salt or Na salt is preferred. As polyhydric alcohol (J2) containing a sulfonic group or its salt, 2,3-bis(hydroxymethyl)benzenesulfonic acid, 3,5-bis(hydroxymethyl)benzenesulfonic acid, 3,4-bis(hydroxymethyl)benzenesulfonic acid, 2,5-bis(hydroxymethyl)benzenesulfonic acid, those salts, etc. are mentioned. As a sulfonate, salts, such as ammonium, Li, Na, K, Mg, Ca, Cu, and Fe, are mentioned. In particular, K salt or Na salt is preferred.

[0032]In polyester resin as negative electrification control resin contained in a toner of this invention, Quantity of polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group or its salt and/or a sulfonic group, or its salt, a total monomer (sum total of all the carboxylic acid components and all the alcohol components) which constitutes polyester resin — usually — 0.2–30-mol % — it is 0.5–10-mol % preferably. By containing this polyvalent-carboxylic-acid compound (J1) and/or polyhydric alcohol (J2) as a polycondensation ingredient, the dispersibility of paints in a toner can improve and the electrostatic property of a toner can be controlled.

[0033]Here, in a toner of this invention, although right electrification control resin and negative electrification control resin are used together, the rates differ by whether a toner is made into positive triboelectric charging, or it is considered as negative triboelectric charging. An amino group which brings about positive triboelectric charging in right electrification control resin in obtaining a positive triboelectric charging toner, or the number of mol equivalents of the salt. (it is hereafter called a "right functional group amount".) — content in a toner of each electrification control resin is adjusted so that it may increase more than the number of mol equivalents of a sulfonic group which brings about negative triboelectric charging in negative electrification control resin, or its salt (henceforth "a negative functional group amount"). In obtaining a negative triboelectric charging toner, a negative functional group amount adjusts a using rate of each electrification control resin so that it may increase more than a right functional group amount.

[0034]The right functional group amount P a product of weight % of an amino group which brings about positive triboelectric charging in "right electrification control resin, or its salt, and a right electrification control resin amount in a toner specifically, It is computable as what $\frac{P}{Q}$ (ed)" with a molecular weight of a structural unit which has an amino group which brings about positive triboelectric charging in right electrification control resin, or its salt. The negative functional group amount Q "a product of weight % of a sulfonic group which brings about negative triboelectric charging in negative electrification control resin, or its salt, and a negative electrification control resin amount in a toner, It is computable as what $\frac{Q}{P}$ (ed)" with a molecular weight of a structural unit which has a sulfonic group which brings about negative triboelectric charging in negative electrification control resin, or its salt. a case of a positive triboelectric charging toner — a ratio (P:Q) of the right functional group amount P and the negative functional group amount Q — usually — 1:0.005 to 1:0.9 — desirable — 1:0.01 to 1:0.8 — it is determined that it is more preferably set to 1:0.05 to 1:0.7 by rate of each electrification control resin. a case of a negative triboelectric charging toner — a ratio (Q :P) of the negative functional group amount Q and the right functional group amount P — usually — 1:0.005 to 1:0.9 — desirable — 1:0.01 to 1:0.8 — it is determined that it is more preferably set to 1:0.05 to 1:0.7 by rate of each electrification control resin. In this functional group amount ratio, when one ratio was too small and continuous printing is carried out, fault of that an electrification controllability becomes high too much and printing endurance and printing density fall, a toner dispersing may be produced. On the contrary, when one ratio is too large, electrostatic property may become insufficient and problems, such as fogging, may be produced.

[0035]In this invention, by using together negative electrification control resin and right electrification control resin, By using together by said functional group ratio desirably, electrostatic property seldom changes also in which environment under low-humidity/temperature and high-humidity/temperature, but further, even if it performs continuous printing, a toner with which deterioration of image quality and generating of fogging are controlled

can be obtained.

[0036]A toner of this invention is the sum total, and is usually carrying out 0.03–10 weight-section content of polyester resin as right electrification control resin, and the polyester resin as negative electrification control resin preferably 0.01 to 20 weight section to the binding resin 100 below-mentioned weight section. If there is little quantity of polyester resin, electrification controlling performance will not appear, but if too large, variation width of electrification quantity by an environmental variation will become large easily.

[0037]Even if a toner of this invention does not use other charge controlling agents together other than polyester resin mentioned above, it shows practically sufficient electrifying characteristic. However, the conventional charge controlling agent may be used together for the purpose, such as fine adjustment. It is possible to use a charge controlling agent of various kinds of positive triboelectric charging or negative triboelectric charging as other charge controlling agents. For example, a metal complex of an organic compound which has a carboxyl group or a nitrogen-containing basis, metallized dye, Nigrosine, etc. are mentioned. More specifically SUPIRON black TRH (made by the Hodogaya chemical industry company), T-77 (made by the Hodogaya chemical industry company), BONTORON S-34 (made by an Orient chemical industry company), BONTORON E-84 (made by an Orient chemical industry company), BONTORON N-01 (made by an Orient chemical industry company), other electrification control resin, such as charge controlling agents, such as copy blue PR (made by Clariant, LTD.), and/or the 4th class ammonium (salt) group content (meta-) acrylate system copolymer, and a sulfonic acid (salt) group content acrylate system copolymer, can be mentioned.

[0038]A polymer currently used for usual can be used for binding resin contained in this invention toner as binding resin of a toner. Specifically Polystyrene, styrene (meta) acrylate copolymerization resin, Polyester resin other than the above, polyurethane, an epoxy resin, polyolefine, A core hydrogenation thing of polyamide, polysulfone, polish anoa reel ether, acrylate (meta) resin, norbornene system resin, and styrene resin, a core hydrogenation thing of styrene isoprene styrene block polymer, etc. are mentioned.

[0039]As colorant contained in a toner of this invention, there are black colorant, a yellow coloring agent, a magenta coloring agent, cyanogen colorant, etc. As black colorant, magnetic particle [such as carbon black, the dyes-and-pigments; cobalt of the Nigrosine base, nickel, a tri-iron tetraoxide, iron oxide manganese, iron oxide zinc and iron oxide nickel,]; etc. can be mentioned. When using carbon black, since good image quality will be obtained and safety to environment of a toner will also increase if primary particle diameter uses what is 20–40 nm, it is desirable. As a yellow coloring agent, compounds, such as azo pigment and condensed polycyclic pigment, are used. Specifically, the C.I. pigment yellow 3, 12, 13, 14, 15, 17, 62, 65, 73, 83, 90, 93, 97, 120, 138, 155, and 180 and 181 grades are mentioned. As a magenta coloring agent, compounds, such as azo pigment and condensed polycyclic pigment, are used. Specifically The C.I. pigment red 48, 57, 58, 60, 63, 64, 68, 81, 83, 87, 88, 89, 90, 112, 114, 122, 123, 144, 146, 149, 163, 170, 184, 185, 187, 202, 206, 207, and 209, 251, the C.I. pigment violet 19, etc. are mentioned. As cyanogen colorant, a copper-phthalocyanine compound and its derivative, an anthraquinone compound, etc. can be used. Specifically, the C.I. pigment blues 2, 3, 6, 15, 15:1, 15:2, 15:3, 15:4, 16, and 17 and 60 grades are mentioned. Quantity of these colorant is usually one to 20 weight section preferably 0.1 to 50 weight section to binding resin 100 weight section.

[0040]A toner of this invention may contain a release agent from viewpoints of an improvement of low temperature fixability, prevention from filming, etc. As a release agent, for example Low molecular weight polyethylene, low molecular weight polypropylene, Polyolefine waxes, such as low-molecular-weight polybutylene; Candelilla, Vegetable system natural wax, such as carnauba, rice, and haze wax; Paraffin, Synthetic waxes, such as petroleum system wax; Fischer Tropsch waxes, such as micro crystalline and PETORO lactam; Pentaerythritol tetra Millis Tait, Polyfunctional ester compounds, such as pentaerythritol tetra palmitate and dipentaerythritol hexa Millis Tait, etc. are mentioned. These can be used combining one sort or two sorts or more.

[0041]A synthetic wax (especially the Fischer Tropsch wax), a petroleum system wax, a polyfunctional ester compound, etc. are [among these] preferred. In a DSC curve measured with a

differential scanning calorimeter also in these, Endothermic peak temperature at the time of temperature up preferably 30–200 ** 50–180 **, Polyfunctional ester compounds, such as pentaerythritol ester which is in the range of 60–160 ** preferably especially, and dipentaerythritol ester in a range in which the endothermic peak temperature is 50–80 **, are preferred especially in respect of fixing-detachability balance as a toner. A molecular weight is especially 1000 or more, five or more weight sections dissolve at 25 ** to styrene 100 weight section, and, as for dipentaerythritol ester which is 10 or less mg/KOH, acid value shows higher efficacy to a fixing temperature fall. Endothermic peak temperature is the value measured by ASTM D3418–82. Quantity of the above-mentioned release agent is usually one to 15 weight section preferably 0.1 to 20 weight section to binding resin 100 weight section.

[0042] 1–10 micrometers of volume average particle diameter (dv) of a toner of this invention are usually 3–8 micrometers preferably — a ratio (dv/dp) of volume average particle diameter to number average particle diameters (dp) — 1–2.0 — it is 1–1.5 preferably. It is preferred that ranges of a value (rl/rs) which broke the major axis rl of a toner by the minor axis rs are 1–1.3. When this ratio becomes large, transfer nature which transfers a toner image on a photo conductor to transfer materials, such as paper, may fall, or since friction between toners becomes large when this toner is dedicated to a toner compartment of an image forming device, an external additive may exfoliate, and endurance may fall.

[0043] a toner of this invention — melt viscosity in 120 ** — usually — 10,000 or less Pa·s — desirable — 100–10,000 Pa·s — it is 1,000 – 8,000 Pa·s more preferably. According to the toner with such melt viscosity, high definition is realized also by printing at a high speed. Measurement of viscosity can be measured using a flow tester. 50–80 ** of softening temperature by a flow tester is usually 60–70 ** preferably, and 90–150 ** of outflow starting temperature is usually 100–130 ** preferably. When softening temperature is low, preservability may fall, and when conversely high, fixability may fall. When outflow starting temperature is low, hot offset tolerance may fall, and when conversely high, fixability may fall. 0–80 ** of glass transition temperature according [a toner of this invention] to a differential scanning calorimeter is usually 40–70 ** preferably. When glass transition temperature is low, preservability may fall, and when conversely high, fixability may fall.

[0044] A tetrahydrofuran (THF) insoluble daily dose of a toner of this invention is usually 0 to 20% preferably 0 to 50%. A fall of a gross and aggravation of transparency occur in not less than 50%. A THF insoluble daily dose can be measured by a below-mentioned method. a volume specific resistance value (log (ohm·cm)) according [a desirable toner used for this invention] to a dielectric loss measuring instrument — usually — 10–13 — it is a thing of 10.5–12.5 preferably. When a volume specific resistance value is small, fogging may occur, and when conversely large, toner scattering, fogging, filming, or cleaning defect may occur. As for a toner of this invention, it is preferred that there is little electrification quantity change in a high-humidity/temperature environment (H/H environment) and low-humidity/temperature environment (L/L environment) and that what is called environmental stability is high. As for variation of electrification quantity between each environment, in that case, it is preferred that it is below 5 microC/g. When environmental stability is low, fogging may occur.

[0045] A toner of this invention has the preferred number of color particles with a major axis of 0.2 micrometers or more observed in an area of 100 micrometers x 100 micrometers of a toner which carried out heat melting and was made into 20 micrometers of thickness in their being 50 or less pieces, it is more preferred in their being 30 or less pieces, and is still more preferred in their being 20 or less pieces. If there are many these numbers, it will get bad to the spectral characteristics, such as transparency required for reappearance of a clear color tone of a color picture, and fogging may increase and printing density may become low. The spectral characteristic can perform solid printing with a commercial printer, and can measure the color tone with a spectrum color difference meter.

[0046] The toner of this invention can make the exterior of a toner mentioned above particles of core shell structure (it is also called capsule structure) by covering with other polymers. By intension-izing internal (core layer) low softening point material in core shell structure particles by a substance which has softening temperature higher than it, since low-temperature-izing of

fixing temperature and prevention from condensation at the time of preservation can be balanced, it is desirable.

[0047]In the case of a core shell type toner, 0–80 ** of glass transition temperature of a polymer which constitutes a core layer is usually 40–60 ** preferably. When glass transition temperature is too high, fixing temperature may become high, and when too conversely low, preservability may fall. It is necessary to set up glass transition temperature of a polymer which constitutes a shell layer become higher than glass transition temperature of a polymer which constitutes a core layer as binding resin. Glass transition temperature of a polymer which constitutes a shell layer is 50–130 ** usually 80–110 ** more preferably 60–120 ** in order to raise the preservability of a toner. When lower than this, preservability may fall, and when conversely high, fixability may fall. Not less than 20 ** of differences of glass transition temperature of a polymer which constitutes a core layer, and glass transition temperature of a polymer which constitutes a shell layer are not less than 10 ** usually not less than 30 ** more preferably. When smaller than this difference, balance of preservability and fixability may fall.

[0048]Especially a wt. ratio of a core layer of a core shell type toner and a shell layer is usually use **** at 80 / 20 – 99.9/0.1, although not limited. If a rate of a shell layer is smaller than the above-mentioned rate, preservability will worsen, and conversely, if larger than the above-mentioned rate, it will become difficult to be established at low temperature.

[0049]It is desirable to restrict the amount of residual metals (ion) in a toner furthermore. When metal (ion), such as magnesium and calcium, remains in a developer especially, under a high-humidity condition, moisture absorption may be caused, the mobility of a developer may be reduced and it may have an adverse effect on image quality. What has few content in a developer of magnesium or calcium (only henceforth residual metals) can give good image quality without high printing density and fogging also under a high-humidity/temperature condition with a high speed machine which can print 30 or more sheets in 1 minute. 170 ppm or less of the amounts [150 ppm or less of] of residual metals are 120 ppm or less especially preferably more preferably. What is necessary is to dry using washing dehydrators, such as a continuous system belt filter and a siphon peeler type centrifuge, etc., to repeat and perform washing, and just to dry, for example in a drying stage of a toner production process, in order to reduce residual metals.

[0050]A toner of this invention, for example in thermoplastics used as ** binding resin ingredient, After carrying out melting mixing of colorant, right electrification control resin, negative electrification control resin, the release agent, etc., making it distribute uniformly and considering it as a constituent, A toner by grinding and classifying this constituent in a polymerization nature monomer which is pulverizing method and ** binding resin raw material to obtain Colorant, Right electrification control resin, negative electrification control resin, a release agent, etc. are dissolved or distributed, The drainage system carrier fluid inside of the body containing dispersion stabilizer is distributed after adding a polymerization initiator, Particles of binding resin obtained by the polymerizing method and ** emulsion polymerization which obtain a toner by warming to prescribed temperature, starting a polymerization, and filtering, washing, drying and drying after an end of a polymerization, distributed polymerization, etc., Particles containing colorant, right electrification control resin, and negative electrification control resin, The meeting method for obtaining a toner by filtering particles made to meet and drying, ** Hydrophilic radical content resin is used as binding resin, and after adding colorant, right electrification control resin, negative electrification control resin, etc. to it and making it dissolve in an organic solvent, it can manufacture by neutralizing this resin and drying phase inversion and after that with a phase inversion emulsification method etc. which obtain a toner. A toner obtained from a viewpoint of obtaining a toner which gives dot reproducibility good image quality also in this, by the polymerizing method is preferred.

[0051]Right electrification control resin 100 weight section which consists of polyester resin in which a manufacturing method of a toner of this invention carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing an amino group mentioned above or its salt and/or an amino group, or its salt, Ten to colorant 200 weight section and zero to organic solvent 100 weight section which may dissolve this

electrification control resin are mixed, Negative electrification control resin 100 weight section which consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing a process of obtaining a right electrification control resin composition, a sulfonic group mentioned above, or its salt and/or a sulfonic group, or its salt, Ten to colorant 200 weight section and zero to organic solvent 100 weight section which may dissolve this electrification control resin are mixed, and it has the process of obtaining a negative electrification control resin composition. In a manufacturing method of a toner of this invention, it is preferred to use an electrification control resin composition produced by mixing positive or negative electrification control resin 100 weight section, and 20 to colorant 150 weight section. By manufacturing a toner using an electrification control resin composition, colorant can be uniformly distributed in a toner.

[0052]If an organic solvent is used in manufacture of positive or a negative electrification control resin composition used by this invention, since electrification control resin can be dissolved or swollen, it can mix in the state where resin is soft and colorant can be distributed uniformly, it is desirable. When not using an organic solvent, there is a thing with which resin warms and is not mixed to temperature which is a grade which becomes soft and which it is necessary to carry out and control of temperature becomes difficult. Since an organic solvent may evaporate by warming when especially the boiling point of an organic solvent is low when using an organic solvent, it is a room temperature or it is preferred to cool and to obtain positive or a negative electrification control resin composition. As for an organic solvent, since a problem of a bad smell may occur when an organic solvent remains in a toner, it is preferred to be removed in either at the time of manufacture of positive or a negative electrification control resin composition or manufacture of a toner. If quantity of an organic solvent is ten to 60 weight section and is in this range still more preferably five to 80 weight section preferably zero to 100 weight section to positive or negative electrification control resin 100 weight section, balance of dispersibility and processability is excellent. Checking a kneading state, even if an organic solvent adds the whole quantity at once at this time, it may divide into several times and may add.

[0053]When using an organic solvent, the solubility coefficient (henceforth an SP value) is $8 - 15 [\text{cal}/\text{cm}^3]^{1/2}$, and a thing of a range whose boiling point is 50–150 ** is preferred. If an SP value is smaller than $8 [\text{cal}/\text{cm}^3]^{1/2}$, polarity can become small and electrification control resin may be dissolved, If an SP value is conversely larger than $15 [\text{cal}/\text{cm}^3]^{1/2}$, polarity can become high and electrification control resin may be dissolved. On the other hand, when the boiling point is lower than 50 **, an organic solvent may evaporate with heat generated by kneading, and when conversely higher than 150 **, it may become difficult after kneading to remove an organic solvent. As an organic solvent, concretely (an SP value/boiling point) Methanol (14.5/65 **), Ethanol (10.0/78.3 **), propanol (11.9/97.2 **), A diethyl ketone (8.8/102 **), di-n-propyl ketone (8.0/144 **), Di-iso-propyl ketone (8.0/124 **), methyl-n-propyl ketone (8.3/102 **), Methyl-iso-propyl ketone (8.5/95 **), methyl-n-butyl ketone (8.5/127 **), Methyl-iso-butyl ketone (8.4/117 **), toluene (8.9/110 **), A tetrahydrofuran (9.1/65 **), methyl ethyl ketone (9.3/80 **), acetone (9.9/56 **), cyclohexanone (9.9/156 **), etc. are mentioned, and these may be used independently, or may mix and use two or more sorts. Also in this, in consideration of solubility to electrification control resin, and removal after kneading, a diethyl ketone, Methyl-n-propyl ketone, methyl-n-butyl ketone, toluene / methanol mixed solvent, toluene / ethanol mixed solvent, toluene / propanol mixed solvent, and methyl ethyl ketone / methanol mixed solvent are preferred.

[0054]Mixing can be performed using a roll, a PURASUCHI coder (made by the Brabender company), a lab PURASUTO mill (made by an Oriental energy machine company), a kneader, a 1 axis extrusion machine, a twin screw extruder, Banbury, the Bus ko kneader, etc. Since there are a bad smell and a toxic problem when using an organic solvent, a mixer of a sealing system in which an organic solvent does not leak is preferred. Since that a torque meter is installed in a mixer can manage dispersibility on a level of torque, it is preferred.

[0055]Positive or a negative electrification control resin composition used by this invention,

After adding an organic solvent to this constituent and considering it as 5% of resin solution, on a glass plate, The number of color particles with a major axis of 0.2 micrometers or more observed in an unit area of 100 micrometers x 100 micrometers of a film from which a gap is obtained by applying and drying a resin solution with a doctor blade which is 30 micrometers is preferred in their being 20 or less pieces, more preferred in their being ten or less pieces, and still more preferred in their being five or less pieces. If there are many these numbers, it will get bad to the spectral characteristics, such as transparency required for reappearance of a clear color tone of a color picture, and fogging may increase and printing density may become low. The spectral characteristic performs solid printing with a commercial printer, and measures the color tone with a spectrum color difference meter. After adding an organic solvent and considering it as 5% of resin solution, a gap applies a mixed solution on a glass plate with a doctor blade which is 30 micrometers, When the number of color particles with a major axis of 0.2 micrometers or more observed in an unit area of 100 micrometers x 100 micrometers of a film produced by drying uses positive [20 or less] or a negative electrification control resin composition, Heat melting can be carried out, it can be made 20 micrometers of thickness, and the number of color particles with a major axis of 0.2 micrometers or more observed in an area of 100 micrometers x 100 micrometers can obtain comparatively easily a toner which is 50 or less pieces.

[0056]In a manufacturing method of a toner of this invention, in order to make positive or a negative electrification control resin composition include in a toner, After carrying out melt kneading of the other additive agents etc. binding resin, this electrification control resin composition, and if needed, in pulverizing method and a suitable drainage system carrier fluid body which are ground and classified so that it may become the particle size distribution of an after-cooling request. Although the polymerizing method etc. which polymerize a polymerization nature monomer used as a raw material of binding resin, an electrification control resin composition, and a polymerization nature monomer composition that contains other additive agents if needed are mentioned, since a toner which gives dot reproducibility good image quality is obtained, manufacturing by the polymerizing method is preferred.

[0057]In a manufacturing method of a toner of this invention, said 0.1 to right electrification control resin composition 20 weight section, It is preferred to mix 0.1 to 20 weight section of a negative electrification control resin composition and polymerization nature monomer 100 weight section, to obtain a polymerization nature monomer composition, to polymerize this in a drainage system carrier fluid body, and to manufacture a toner. A rate of a right electrification control resin composition and a negative electrification control resin composition is whether a toner is made into positive triboelectric charging, or to consider it as negative triboelectric charging, and it can be suitably changed so that it may become the functional group amount ratio mentioned above.

[0058]Although a polymerization method in particular may not be limited but any of an emulsion polymerization, suspension polymerization, a distributed polymerization, and soap free polymerization may be sufficient, From a point which can make colorant able to contain uniformly and can raise electrostatic property and transfer nature, a suspension polymerization method is preferred and specifically, A polymerization nature monomer, a right electrification control resin composition, a negative electrification control resin composition, a regulator, a release agent, and a polymerization nature monomer composition that contains additive agents, such as a charge controlling agent, if needed are polymerized in a drainage system medium.

[0059]Hereafter, a manufacturing method of a core shell type toner by more desirable suspension polymerization is explained. In a drainage system carrier fluid body to contain, a dispersion stabilizing agent A polymerization nature monomer (polymerization nature monomer for cores), By making a polymerization nature monomer composition (monomer composition for cores) containing a right electrification control resin composition, a negative electrification control resin composition, and other additive agents suspended, and polymerizing using a polymerization initiator, A core particle can be manufactured, a polymerization nature monomer (polymerization nature monomer for shell) and a polymerization initiator for forming shell can be added further, and capsule toner can be obtained by polymerizing. How to add a polymerization nature monomer for shell to the system of reaction of a polymerization reaction which obtains

said core particle and which was performed for accumulating, and polymerize continuously in it as a concrete method of forming shell, Or a core particle obtained by another system of reaction can be taught, and a method of adding a polymerization nature monomer for shell to this, and polymerizing gradually in it, etc. can be mentioned. It can add collectively in the system of reaction, or a monomer for shell ingredients can be added continuously or intermittently using pumps, such as a plunger pump.

[0060]As a polymerization nature monomer for cores, a monovinyl system monomer, a cross-linking monomer, a macro monomer, etc. can be mentioned. This polymerization nature monomer polymerizes and it becomes a binding resin ingredient. As a monovinyl system monomer, specifically Styrene, vinyltoluene, styrene monomer [, such as alpha-methylstyrene,]; (meta-) — acrylic acid; (meta-) — methyl acrylate. (Meta) Ethyl acrylate, acrylic acid (meta) propyl, butyl acrylate (meta), (Meta) 2-ethylhexyl acrylate, acrylic acid (meta) cyclohexyl, (Meta) A derivative of acrylic acid (meta), such as acrylic acid iso BONIRU, acrylic acid (meta) dimethylaminoethyl, and acrylamide (meta); monoolefin system monomer [, such as ethylene, propylene, and butylene,]; etc. are mentioned. A monovinyl system monomer may be used independently or may be used combining two or more monomers. Concomitant use with styrene monomer independence, a styrene monomer, and a derivative of acrylic acid (meta), etc. are suitably used among these monovinyl system monomers.

[0061]If a cross-linking monomer and a polymer are used with a monovinyl system monomer, it is effective in a hot offset improvement. A cross-linking monomer is a monomer which has a carbon-carbon unsaturated double bond which can polymerize two or more. Specifically Aromatic divinyl compound; ethylene glycol dimethacrylate, such as divinylbenzene, divinylanthracene, and these derivatives, Diethylene nature unsaturated carboxylic acid ester, such as diethylene-glycol dimethacrylate; N,N-divinylaniline, A compound etc. which have three or more vinyl groups which have two vinyl groups, such as divinyl ether, such as a compound, pentaerythritol triaryl ether, and trimethylolpropane triacrylate, can be mentioned. In a polymer, a cross-linking polymer is two or more vinyl groups a polymer which it has, and specifically, Ester obtained by carrying out the condensation reaction of polymers which have two or more hydroxyl groups, such as polyethylene, polypropylene, polyester, and a polyethylene glycol, and the unsaturated carboxylic acid monomers, such as acrylic acid and methacrylic acid, to intramolecular can be mentioned. These cross-linking monomers and a cross-linking polymer are independent, respectively, or can be combined two or more sorts and can be used. Ten or less weight sections of the amount used are usually 0.1 – the amount part of duplexes preferably per monovinyl system monomer 100 weight section.

[0062]If a macro monomer is used with a monovinyl system monomer, since balance of preservability and low temperature fixability will become good, it is desirable. A macro monomer has a vinyl polymerization nature functional group at the end of a chain, and a number average molecular weight is usually oligomer or polymer of 1,000–30,000. If what has a small number average molecular weight is used, a surface portion of a polymer particle will become soft and preservability will come to fall. Conversely, if what has a large number average molecular weight is used, the melting nature of a macro monomer will worsen and fixability and preservability will come to fall. As a vinyl polymerization nature functional group in an end of a macro monomer chain, an acrylyl group, a methacryloyl group, etc. can be mentioned and a methacryloyl group is preferred from a viewpoint of the ease of carrying out of copolymerization.

[0063]As for a macro monomer, what has a glass transition temperature higher than glass transition temperature of a polymer produced by polymerizing said monovinyl system monomer is preferred. As an example of a macro monomer used for this invention, Although it is independent in styrene, a styrene derivative, methacrylic acid ester, acrylic ester, acrylonitrile, a methacrylonitrile, etc. or a polymer produced by polymerizing two or more sorts, a macro monomer which has a polysiloxane skeleton, etc. can be mentioned, A polymer produced by being independent or polymerizing combining these also in it in a thing especially methacrylic acid ester, or acrylic ester of hydrophilic nature is preferred. when using a macro monomer, the quantity receives monovinyl system monomer 100 weight section — usually — it is 0.05 to 1 weight section still more suitably 0.03 to 5 weight section suitably 0.01 to 10 weight section. If

there is little quantity of a macro monomer, the preservability of a toner will not improve. If quantity of a macro monomer increases extremely, the fixability of a toner will come to fall. [0064]Also in a polymerization nature monomer for cores, that in which glass transition temperature can usually form 60 ** or less of 40-60 ** polymers preferably is preferred as a monomer for cores. If glass transition temperature is too high, fixing temperature will become high, and if too conversely low, the preservability of a toner will fall. Usually, a monomer for cores may be used combining one sort or two sorts or more.

[0065]It is desirable that it is what gives a polymer which has a glass transition temperature higher than glass transition temperature of a polymer which constitutes a core particle as a polymerization nature monomer for shell. It is independent, respectively, or two or more sorts of monomers which form a polymer with glass transition temperature of greater than 80 **, such as styrene, acrylonitrile, and methyl methacrylate, as a monomer which constitutes a polymerization nature monomer for shell can be used, combining them. Glass transition temperature of a polymer obtained by a polymerization nature monomer for shell is 50-130 ** usually 80-110 ** more preferably 60-120 ** in order to raise the preservation stability of polymerization toner. When lower than this, preservation stability may fall, and when conversely high, fixability may fall. Not less than 20 ** of differences of glass transition temperature between a polymer which consists of a polymerization nature monomer for cores, and a polymer which consists of a polymerization nature monomer for shell are not less than 10 ** usually not less than 30 ** more preferably. If smaller than this difference, preservability will fall.

[0066]As a polymerization initiator, persulfate; 4,4'-azobis, such as potassium persulfate (4-cyanovaleric acid), 2,2'-azobis (2-methyl-N-(2-hydroxyethyl) propionamide.) 2 and 2'-azobis (2-amidinopropane) dihydrochloride, Azo compounds, such as 2,2'-azobis (2,4-dimethylvaleronitrile) and 2,2'-azobisisobutyronitrile; Lauroyl peroxide, Benzoyl peroxide, t-butylperoxy 2-ethylhexanoate, t-hexyl peroxy 2-ethylhexanoate, t-butylperoxy perpivalate, Peroxides, such as di-isopropyl peroxy dicarbonate, 1, 1 and 3, and 3-tetramethyl butylperoxy 2-ethylhexanoate and t-buthylperoxy isobuthylate, can be illustrated.

[0067]Also in these, it is preferred to choose an oil-soluble polymerization initiator as a polymerization nature monomer composition for cores, and it is preferred to choose a water-soluble polymerization initiator as a polymerization nature monomer composition for shell. A polymerization initiator for cores is **** for 0.5 - 10 weight sections still more preferably 0.3 to 15 weight section preferably 0.1 to 20 weight section to monovinyl system monomer 100 weight section. A polymerization initiator can also be added to suspension after an end of a granulation stage depending on the case, although it can add beforehand in a polymerization nature monomer composition. Quantity of a polymerization initiator for shell is a drainage system medium standard, and is usually 0.001 to 1 % of the weight. If this is small, a polymerization will not progress, but productivity falls, if conversely large, a molecular weight will fall and preservability will worsen.

[0068]In order to polymerize stably, dispersion stabilizer can be added to reaction mixture. As dispersion stabilizer, for example Sulfate; barium carbonate, such as barium sulfate and calcium sulfate, Phosphates, such as carbonate; calcium phosphate, such as calcium carbonate and magnesium carbonate; An aluminum oxide, Metallic compounds, such as metallic-oxides [, such as titanium oxide,], and aluminium hydroxide, Water soluble polymers, such as metal hydroxide; polyvinyl alcohol, such as magnesium hydroxide and a ferric hydroxide, methyl cellulose, and gelatin; an anionic surface-active agent, a nonionic surface-active agent, an ampholytic surface active agent, etc. can be mentioned, and these may be used independently or may use two or more kinds together. The dispersion stabilizer containing colloid of metallic compounds, especially metal hydroxide of difficulty water solubility can narrow particle size distribution of a polymer particle, and there is little ullage after washing of a dispersing agent, and since it can reproduce a picture vividly, it is [among these] preferred.

[0069]Dispersion stabilizer containing colloid of difficulty water solubility metal hydroxide, Colloid of metal hydroxide of difficulty water solubility obtained by adjusting the pH of solution of a water-soluble polyvalent metal compound to seven or more although there is no restriction by the process, It is preferred to use colloid of metal hydroxide of difficulty water solubility

especially generated by the reaction in aqueous phase of a water-soluble polyvalent metal compound and hydroxylation alkali metal salt.

[0070]As for colloid of difficult water soluble metallic compounds, in number particle size distribution, it is preferred that particle diameter D_{p90} particle diameter D_{p50} whose number total which measured from the diameter side of a granule is 50% is 0.5 micrometer or less, and is [90] 90% is 1 micrometer or less. If particle diameter of colloid becomes large, the stability of a polymerization will collapse and the preservability of a toner will fall.

[0071]A dispersion stabilizing agent is usually used at a rate of 0.1 to 20 weight section to monovinyl system monomer 100 weight section. If there are few these rates than 0.1 weight sections, it will be difficult to acquire sufficient polymerization stability, and will become easy to generate a polymerization aggregate. On the contrary, if 20 weight sections are exceeded, toner particle diameter after a polymerization becomes fine too much, and is not practical.

[0072]As a regulator, halogenated hydrocarbon [, such as mercaptans; carbon tetrachlorides, such as t-dodecyl mercaptan, n-dodecyl mercaptan, and n-octyl mercaptan, and carbon tetrabromide,]; etc. can be mentioned, for example. These regulators can be added in the middle of a polymerization before a polymerization start. A regulator is usually preferably used at a rate of 0.1 to 5 weight section 0.01 to 10 weight section to monovinyl system monomer 100 weight section.

[0073]Although a toner of this invention remains as it is and is also applicable to development of electro photography, in order to adjust the electrostatic property of a toner, mobility, preservation stability, etc., it usually uses them for it, making particles (henceforth an external additive) of particle diameter smaller than this particle toner adhere or lay under the toner particle surface. An inorganic particle and organic resin particles are mentioned as an external additive. As an inorganic particle, a silica dioxide, an aluminum oxide, titanium oxide, a zinc oxide, tin oxide, barium titanate, strontium titanate, etc. are mentioned. As organic resin particles, methacrylate polymer particles, acrylic ester polymer particles, Core shell type particles etc. in which styrene methacrylic-acid-ester copolymer particles, styrene acrylic ester copolymer particles, zinc stearate, calcium stearate, and shell were formed in with a methacrylic-acid-ester copolymer, and a core was formed with a styrene polymer are mentioned. In the case of a magnetic one component system developer, oxides, such as iron, cobalt, nickel, an alloy that makes them a subject, or a ferrite, may also be included. An inorganic oxide particle, especially silica dioxide particles are [among these] preferred. Especially silica dioxide particles by which could carry out hydrophobing processing of these particle surfaces, and hydrophobing processing was carried out are preferred. Although quantity in particular of an external additive is not limited, it is usually 0.1 to 6 weight section to particle toner 100 weight section. An external additive may be used combining two or more sorts. When using combining an external additive, a method of combining the inorganic particles or an inorganic particle which differs in mean particle diameter, and organic resin particles is preferred. In order to make an external additive adhere to said particle toner, it teaches mixers, such as a Henschel mixer, and an external additive and particle toner are agitated and are usually performed. In adjusting a toner with an underwater polymerization mentioned above, after carrying out the agitation mix of the external additive to a water dispersing element of moisture handbill particle toner, a wet method, such as carrying out spray desiccation, can also be used.

[0074]

[Example]Next, although an example is given and this invention is explained in detail, this invention is not limited to these examples. The part in these examples and % are weight references as long as there is no special mention. It evaluated by this example by the following methods.

1. A polyester resin characteristic (1) number average molecular weight, the number average molecular weight of weight-average-molecular-weight polyester, and weight average molecular weight were computed as a standard polystyrene equivalent unit in accordance with the GPC method.

(2) The hydroxyl value of hydroxyl value polyester was measured according to the method indicated in 2, 4 and 9 of "standard fats-and-oils assay method" (Japanese oil recovery study

association), and 2 -83 paragraph. A unit is mgKOH/g.

(3) The glass transition temperature (T_g) of glass-transition-temperature polyester resin was measured according to the DSC method specified to JIS K 7121. A unit is **.

[0075]2. After taking out some of electrification control resin composition characteristic (1) colorant-dispersibility 1 positive or negative electrification control resin compositions, the toluene which dissolves electrification control resin was added and it was made the 5% solution of the electrification control resin composition. On the glass plate, the gap applied and dried the mixed solution with the doctor blade which is 30 micrometers, and produced the film. The major axis which observes this sheet with an optical microscope and exists in 100-micrometer square counted the number of a color particle of 0.2 micrometers or more.

[0076]3. The volume average particle diameter (d_v) and number average particle diameters (d_p) of the particle diameter toner of the toner characteristic (1) toner were measured by the multi-sizer (made by Beckman Coulter). Measurement by this multi-sizer was performed on diameter:of aperture100micrometer, the medium:iso ton II, and measurement-particles number:100000 piece conditions.

(2) The shape of the toner shape toner measured the value (r_l/r_s) which took the photograph with the scanning electron microscope, read the photograph with the nexus 9000 type image processing device, and broke the major axis of the toner by the minor axis. The measurement number of the toner at this time was performed by 100 pieces.

(3) Using the melt viscosity flow tester (the Shimadzu make, kind name "CFT-500C"), the amount of samples was set to 1.0-1.3g, it measured by the following measuring condition, and the melt viscosity at 120 ** was measured.

Starting temperature : 35 **, and part [for /] and heating-rate:3 ** preheating time: 5 minutes, cylinder pressure:10.0 Kgf/cm², Dice diameter : 0.5 mm, dice 1.0 mm in length, and 1g of shearing stress:2.451x10⁵Pa(4) THF insoluble daily dose toners are weighed precisely, It puts into a thimble (the ADVANTEC Co., Ltd. make, 86R size of 28x100 mm), and it is applied to Soxhlet extractor, and THF is put into a lower flask and extracted for 6 hours. Extracting solvents were collected after extraction, and in the evaporator, after separation, the soluble pitch extracted in the extracting solvent was weighed precisely, and was computed from the following calculations. A THF insoluble daily dose (%) =(T-S) (/T) x100T: The amount (g) of toner samples

S: The amount (g) of extraction pitches

[0077](5) The volume specific resistance value of a volume specific resistance value toner, About 3 g of toners were put into a tablet molding machine 5 cm in diameter, the specimen was produced, having applied about 100 kg of load for 1 minute, and it was measured under with the temperature of 30 **, and a frequency of 1 kHz conditions using the dielectric loss measuring instrument (the Ando Electric Co., Ltd. make, kind name "TRS-10 type").

(6) The electrification quantity under electrification quantity L/L (temperature of 10 **, 20% of humidity), N/N (temperature of 23 **, 50% of humidity), and H/H (temperature [of 35 **], 80% of humidity) environment was measured, and the situation of the environmental variation was evaluated. The electrification quantity of a toner about a positive triboelectric charging toner. About the printer (the Brother Industries, Ltd. make, trade name "HL1670N") of commercial one ingredient of nonmagnetic development system, and a negative triboelectric charging toner. A toner is put into the printer (offing data company make, trade name "micro line 3010C") of commercial one ingredient of nonmagnetic development system, and five printed patterns of half-tone are printed after neglect under said environment one whole day and night. Then, the toner on a developing roller was attracted to the suction type electrification quantity measuring device, and the electrification quantity per unit weight was measured from electrification quantity and suction quantity.

(7) Optimum dose of toners were put on colorant dispersibility 2 slide glass, the cover glass was hung from on the, it was heated to 170 ** with the hot plate, and melting of the toner was carried out, next power was applied with the cover glass, and the toner was crushed. The major axis which observes the portion whose thickness of the toner measured by the thickness gage

(the ANRITSU CORP. make, trade name:K-402B) is 20 micrometers with an optical microscope, and exists in 100-micrometer square counted the number of a color particle of 0.2 micrometers or more.

[0078]4. The print form was set to the printer which carried out the image evaluation (1) color tone above-mentioned, the toner was put into the developer, the neglect back was performed under the environment (H/H) of the temperature of 35 **, and 80% of humidity, solid printing was performed by concentration 5% one whole day and night, and it measured with the spectrum color difference meter (the Nippon Denshoku Co., Ltd. make, kind name "SE2000").

(2) Set a print form to the printer which carried out the printing density above-mentioned, and a toner is put into a developer, Perform the neglect back under the environment (H/H) of the temperature of 35 **, and 80% of humidity, and continuous printing is performed from the first stage by concentration 5% one whole day and night, Solid printing was performed at the time of the 20,000th sheet printing, black toner used McBeth transmission type image concentration measuring apparatus, color toner used the color reflection type densimeter (X-light company make, kind name "404A"), and printing density was measured.

One whole day and night using the printer which carried out the fogging above-mentioned under the environment (H/H) of the temperature of 35 **, and 80% of humidity (3) After neglect, Perform continuous printing by concentration 5%, and solid printing is performed after 20,000-sheet printing, Printing was stopped on the way, the toner of the nonimage area on the photo conductor after development was stripped off with adhesive tape (Sumitomo 3M make and Scotch whisky mending tape 810-3-18), and it was stuck on a new print form. Black toner measured the whiteness degree (B) of the print form which stuck the adhesive tape with the whiteness degree plan (made by Nippon Denshoku Co., Ltd.), and measured similarly the whiteness degree (A) of the print form which stuck only adhesive tape. Difference deltaY of the whiteness degree (A) and whiteness degree (B) was computed, and it was considered as the fogging value. On the other hand, like black toner, color toner measured the color tone instead of the whiteness degree, expressed as coordinates of Lab space using the above-mentioned spectrum color difference meter, respectively, computed color difference deltaE, and made it the fogging value. The one where this value is smaller shows that there is little fogging.

[0079](4) It converts so that the temperature of the fixing roll part of the printer which carried out the fixing temperature above-mentioned can be changed, the temperature of the fixing roll was changed, by 5 ** unit, the fixing rate of the developer in each temperature was measured, and the fixing examination which asks for the relation between temperature and a fixing rate was done. Since a fixing rate stabilized the temperature of the changed fixing roll, it was neglected 5 minutes or more, and it was calculated from the ratio of the printing density before and behind tape peeling operation about the solid field of the paper which performed solid printing to the print form and was printed to it with the modified printer after that. That is, image concentration in front of ID and after tape exfoliation was carried out ID back, and the fixing rate computed the image concentration before tape exfoliation from the following formula.

fixing rate (%) = (after [ID] / before ID) x 100 — here, tape peeling operation sticks the adhesive tape mentioned above in the measured part of the examination paper, press it, it is made to adhere in a constant pressure, and is a series of operations of exfoliating adhesive tape in the direction which met paper with constant speed, after that. In this fixing examination, fixing roll temperature applicable to 80% of a fixing rate was made into the fixing temperature of a developer.

(5) Fixing roll temperature was changed as well as hot offset temperature fixing temperature measurement, solid printing was performed, and the temperature which hot offset generates was measured. Fixing roll temperature when hot offset occurred was made into hot offset temperature.

[0080][Composition of a hexahydro terephthalic acid screw (beta-hydroxyethyl)] 557 copies of 1,4-cyclohexanedicarboxylic acid and 443 copies of ethylene glycol were taught to the 3 Thu mouth flask provided with an agitator, the thermometer, the flowing-back condenser tube, the water sharing pipe, and the nitrogen gas introducing pipe. It stirs introducing nitrogen gas, and it was made to react at 180 ** for 5 hours, removing the water generated during a reaction.

Reaction temperature was raised to 200 **, the pressure in a flask was reduced little by little, it was made 5 or less mmHg 1.5 hours afterward, the reaction was continued after that for further 2 hours, and the hexahydro terephthalic acid screw (beta-hydroxyethyl) was obtained. The hexahydro terephthalic acid screw (beta-hydroxyethyl) was a water-white fluid.

[0081][Composition of polyester resin]

(Synthetic example 1) In the 3 Thu mouth flask provided with an agitator, the thermometer, the flowing-back condenser tube, the water sharing pipe, and the nitrogen gas introducing pipe. 366 copies of 4-methyl-hexahydrophthalic anhydrides, 100 copies of hexahydro terephthalic acid screws (beta-hydroxyethyl), 100 copies of 5-amino hexahydro isophthalic acid dimethyl ester, 284 copies of 2,2-bis(4-hydroxy cyclohexyl)-propane, and 150 copies of ethylene glycol were taught. The total of a hydroxyl value [X]The total of /acid value The ratio of [Y] is 1.19. It stirs introducing nitrogen gas, and it was made to react at 200 ** for 3 hours, removing the alcohol generated during a reaction. Next, five copies of tetrabutoxy titanate was added, reaction temperature was raised to 220 **, the pressure in a flask was reduced little by little, it was made 5 or less mmHg 1.5 hours afterward, the reaction was continued after that for further 3 hours, and polyester resin (1) was obtained. 10,300 and a hydroxyl value were [the number average molecular weight / 68 mgKOH/g and the glass transition temperature of the obtained polyester resin (1) of 3,100 and weight average molecular weight] 62 **.

[0082](Synthetic example 2) In the 3 Thu mouth flask provided with an agitator, the thermometer, the flowing-back condenser tube, the water sharing pipe, and the nitrogen gas introducing pipe. 366 copies of 4-methyl-hexahydrophthalic anhydrides, 100 copies of hexahydro terephthalic acid screws (beta-hydroxyethyl), 150 copies of 5-sodium sulfoisophtharate dimethyl ester, 234 copies of 2,2-bis(4-hydroxy cyclohexyl)-propane, and 150 copies of ethylene glycol were taught. The total of a hydroxyl value [X]The total of /acid value The ratio of [Y] was 1.11. It stirs introducing nitrogen gas, and it was made to react at 200 ** for 3 hours, removing the alcohol generated during a reaction. Next, five copies of tetrabutoxy titanate was added, reaction temperature was raised to 220 **, the pressure in a flask was reduced little by little, it was made 5 or less mmHg 1.5 hours afterward, the reaction was continued after that for further 3 hours, and polyester resin (2) was obtained. 12,000 and a hydroxyl value were [the number average molecular weight / 52 mgKOH/g and the glass transition temperature of the obtained polyester resin (2) of 3,400 and weight average molecular weight] 63 **.

[0083](Synthetic example 3) 317 copies of hexahydrophthalic acid, 329 copies of terephthalic acid, 304 copies of neopentyl glycol, and 50 copies of trimethylolpropane were taught to the 3 Thu mouth flask provided with an agitator, the thermometer, the flowing-back condenser tube, the water sharing pipe, and the nitrogen gas introducing pipe. The total of a hydroxyl value [X] The total of /acid value The ratio of [Y] is 1.10. It stirs introducing nitrogen gas, and it was made to react at 200 ** for 3 hours, removing the alcohol generated during a reaction. Next, 0.5 copy of zinc acetate was added, reaction temperature was raised to 220 **, the pressure in a flask was reduced little by little, it was made 5 or less mmHg 1.5 hours afterward, the reaction was continued after that for further 3 hours, and polyester resin (3) was obtained. 5,500 and a hydroxyl value were [the number average molecular weight / 72 mgKOH/g and the glass transition temperature of the obtained polyester resin (3) of 2,900 and weight average molecular weight] 53 **.

[0084][Manufacture of a positive electrification control resin composition] (reference example 1) 100 copies of polyester resin (1) obtained in the synthetic example 1 was made to distribute 24 copies of methyl ethyl ketone, and six copies of methanol as electrification control resin, and it kneaded with a roll, cooling. In the place where electrification control resin coiled around the roll, magenta pigment (client company make, trade name "C. I. pigment violet 19") 100 weight section was added gradually, kneading was performed for 1 hour, and the electrification control resin composition (1-1) was manufactured. At this time, a mill opening is 1 mm the first stage. The gap was extended gradually after that, the last was extended to 3 mm, and the organic solvent (methyl-ethyl-ketone/methanol =4/1 partially aromatic solvent) was set by the kneading state of electrification control resin, and was added several times.

After taking out some electrification control resin compositions, add toluene, and it was made to

dissolve and was made the 5% solution of the electrification control resin composition of toluene. On the glass plate, the gap applied and dried the mixed solution with the doctor blade which is 30 micrometers, and produced the sheet. When this sheet was observed with the optical microscope, as for a color particle of 0.2 micrometers or more, the major axis which exists in 100-micrometer square did not exist.

[0085](Reference examples 2-3) As colorant, instead of a magenta pigment (client company make, trade name "C. I. pigment violet 19"), Cyanogen paints (client company make, trade name "C. I. pigment blue 15:3") or a yellow pigment (client company make, trade name "C. I. pigment yellow 180") was used, and also the right electrification control resin composition (1-2 and 1-3) was obtained like the reference example 1. The result of the colorant dispersibility 1 at this time is shown in Table 1.

[0086][Manufacture of a negative electrification control resin composition] (reference examples 4-6) The negative electrification control resin composition (2-1 to 2-3) was obtained like the reference examples 1-3 except having used the polyester resin (2) obtained in the synthetic example 2 instead of polyester resin (1). The result of the colorant dispersibility 1 at this time is shown in Table 1.

[0087][Manufacture of a resin composition] The resin composition (3-1 to 3-3) was obtained like the reference examples 1-3 except having used the polyester resin (3) obtained in the synthetic example 3 instead of polyester resin (1). The result of the colorant dispersibility 1 at this time is shown in Table 1.

[0088]

[Table 1]

【表 1】

顔料の種類 量 (部)	参考例								
	1	2	3	4	5	6	7	8	9
マゼンタ	100	シアン	イエロー	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー
ポリエステル樹脂 (1)	100	100	100	100	100	100	100	100	100
ポリエステル樹脂 (2)				100	100	100			
ポリエステル樹脂 (3)							100		100
樹脂組成物	1-1	1-2	1-3	2-1	2-2	2-3	3-1	3-2	3-3
着色剤分散性 1 (個)	0	0	0	0	0	1	74	63	94

[0089][Manufacture of a toner]

(Example 1) In the solution which dissolved 9.8 copies of magnesium chlorides (water-soluble polyvalent metallic salt) in 250 copies of ion exchange water. It added gradually under stirring of the solution which dissolved 6.9 copies of sodium hydroxide (hydroxylation alkaline metal) in 50 copies of ion exchange water, and magnesium hydroxide colloid (metal hydroxide colloid of difficulty water solubility) dispersion liquid were prepared. Number-average-particle-diameters D50 (50% accumulated of number particle size distribution) and D90 of the drop (90% accumulated of number particle size distribution) measured the particle size distribution of said generated colloid with the size distribution measuring device (the Shimadzu Corp. make, kind name "SALD2000A type"). In measurement by this particle-size-distribution measuring instrument, it carried out on condition of salt solution use 10% as carrier fluid at the time of drop measurement for [refractive-index =1.55-0.20i and ultrasonic-exposure-time =] 5 minutes. 80.5 copies of styrene, 19.5 copies of butyl acrylates, 0.5 copy of divinylbenzene, and a polymethacrylic-acid-ester macro monomer (the Toagosei chemical industry company make.) A trade name "AA6", Tg = The polymerization nature monomer for cores which consists of 0.3 copy of 94 **, Wet milling was performed for 11 copies of right electrification control resin

compositions (1-1) mentioned above, one copy of negative electrification control resin composition (2-1), two copies of t-dodecyl mercaptans, and dipentaerythritol hexa Millis Tait 10 copy using the media type wet grinding mill, and the polymerization nature monomer composition for cores was obtained. On the other hand, two copies of methyl methacrylate and 100 copies of water were micro-disperse-ization-processed with the ultrasonic emulsification machine, and the water dispersion of the polymerization nature monomer for shell was obtained. Dp90 was 1.6 micrometers when the particle diameter of the drop of the polymerization nature monomer for shell was measured with said size distribution measuring device.

[0090] Said monomer composition for cores is fed into the magnesium hydroxide colloidal dispersion liquid obtained with the above, stirring until a drop is stabilized — there — t-butylperoxy2-ethylhexanoate (the Nippon Oil & Fats Co., Ltd. make.) Trade name "par butyl O" After adding five copies, using EBARAMAIRUDA (the Ebara Corp. make, kind name "MDN303V"), quantity shearing stirring during 30 minutes was carried out at the number of rotations of 15,000 rpm, and the drop of the monomer composition was corned. When put the water dispersion of this corned polymerization nature monomer composition for cores into the reactor equipped with stirring wings, a polymerization reaction was made to start at 90 ** and polymerization conversion reached to about 100%, it sampled and the particle diameter of the core was measured. As a result, volume average particle diameter (dv) was 7.3 micrometers. The water dispersion and 2,2'-azobis (2-methyl- N. -(2-hydroxyethyl)- the solution which dissolved 0.2 copy of propionamide (the Wako Pure Chem make, trade name "VA-086") in 65 copies of distilled water was put into the reactor) of said polymerization nature monomer for shell After continuing a polymerization for 8 hours, the reaction was suspended and the water dispersion of pH 9.5 particle toner was obtained.

[0091] After making pH of the system or less into five with sulfuric acid, performing acid cleaning (for 25 ** and 10 minutes) and filtration separating water, stirring the water dispersion of the particle toner obtained with the above, 500 copies of ion exchange water was newly added and re-slurred, and backwashing by water was performed. Then, again, after the repetition line carried out filtering separation of the solid content for drying and backwashing by water several times, the dryer performed 2 day-and-night desiccation at 45 **, and particle toner was obtained. The volume average particle diameter (dv) which took out and measured dry particle toner was 7.3 micrometers, and volume-average-particle-diameter (dv) / number average particle diameters (dp) were 1.21. rl/rs was 1.1 and the amount of gels was 15%. The number of color particles of 0.2 micrometers or more did not have a major axis which exists in an unit area. To 100 copies of particle toner obtained with the above, 0.6 copy of colloidal silica (the Clariant, LTD. make, trade name "HDK2150") by which hydrophobing processing was carried out was added, it mixed to it using the Henschel mixer, and the positive triboelectric charging toner was prepared. The obtained evaluation of the characteristic of a toner, a picture, etc. is shown in Table 2.

[0092] (Examples 2-3) In Example 1, the quantity of the right electrification control resin composition to be used and a negative electrification control resin composition was changed as shown in Table 2, and also the positive triboelectric charging toner was obtained like Example 1. The characteristic of a toner and the evaluation result of a picture which were obtained are shown in Table 2.

[0093] (Comparative examples 1-3) In Example 1, instead of using a right electrification control resin composition and a negative electrification control resin composition, The polymerization nature monomer composition for cores was produced by the formula of Table 2 using the quarternary-ammonium-salt charge controlling agent (Orient chemical industry company make, trade name "BONTORON P-51") as the resin composition (3-1) obtained by the reference example 7, and a charge controlling agent, and also the positive triboelectric charging toner was obtained like Example 1. The obtained evaluation of the characteristic of a toner, a picture, etc. is shown in Table 2. Here, the amount of right charge controlling agents was controlled, and the positive triboelectric charging toner of the comparative examples 1-3 was manufactured so that the electrification quantity which the kind of colorant measures at the same positive triboelectric charging toner of Examples 1-3, and the temperature of 23 ** and 50% of humidity might become

the same.

[0094]

[Table 2]

[表 2]

	実施例			比較例		
	1	2	3	1	2	3
顔料の種類	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー
正帯電樹脂組成物 (1-1)	11					
(1-2)		10.5				
(1-3)			10			
負帯電樹脂組成物 (2-1)	1					
(2-2)		1.5				
(2-3)			2			
樹脂組成物 (3-1)				12		
(3-2)					12	
(3-3)						12
正帯電制御剤				1	1.5	2
トナー特性						
d _v (μm)	7.3	7.1	7.2	7.4	7.2	7.5
d _v /d _p	1.21	1.22	1.21	1.25	1.25	1.28
形状 (r ₁ /r _a)	1.1	1.2	1.1	1.2	1.2	1.3
溶解粘度 (Pa·s)	7400	8100	6900	8500	8600	7900
THF不溶分量 (%)	15	20	18	35	27	36
体積固有抵抗 (log (Ω·cm))	11.4	11.7	11.5	11.6	11.3	11.5
官能基量比 (P:Q)	1:0.09	1:0.15	1:0.21	—	—	—
L/L帯電 (μC/g)	24	26	26	45	38	56
N/N帯電 (μC/g)	24	25	24	24	25	24
H/H帯電 (μC/g)	23	23	22	10	7	22
着色剤分散性 2 (個)	0	1	1	85	71	65
画質評価						
色調 L*	62.2	69.3	95.8	71.6	76.7	95.9
a*	76.9	-19.3	-18.2	51.5	-18.2	-16.8
b*	-28.3	-40.4	83.9	-21.2	-29.3	65.8
印字濃度	1.45	1.48	1.47	1.35	1.38	1.39
カブリ	0.3	0.3	0.7	8.7	14.1	3.6
定着温度 (°C)	130	130	125	145	140	145
オフセット発生温度 (°C)	220	220	220	220	220	220

[0095](Examples 4-6) In Example 1, the quantity of the right electrification control resin composition to be used and a negative electrification control resin composition was changed as shown in Table 2, and also the negative triboelectric charging toner was obtained like Example 1. The characteristic of a toner and the evaluation result of a picture which were obtained are shown in Table 3.

[0096](Comparative examples 4-6) In Example 1, instead of using a right electrification control resin composition and a negative electrification control resin composition, The polymerization nature monomer composition for cores was produced by the formula of Table 3 using the salicylic acid metal salt charge controlling agent (Orient chemical industry company make, trade name "BONTORON E-84") as the resin composition (3-1) obtained by the reference example 7, and a charge controlling agent, and also the negative triboelectric charging toner was obtained like Example 1. The obtained evaluation of the characteristic of a toner, a picture, etc. is shown in Table 3. Here, the amount of negative electrification controlling agents was controlled, and the negative triboelectric charging toner of the comparative examples 4-6 was manufactured so that the electrification quantity which the kind of colorant measures at the same negative triboelectric charging toner of Examples 4-6, and the temperature of 23 ** and 50% of humidity might become the same.

[0097]

[Table 3]

【表 3】

	実施例			比較例		
	4	5	6	4	5	6
顔料の種類	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー
正帯電樹脂組成物 (1-1)	2					
(1-2)		1.5				
(1-3)			1			
負帯電樹脂組成物 (2-1)	10					
(2-2)		10.5				
(2-3)			11			
樹脂組成物 (3-1)				12		
(3-2)					12	
(3-3)						12
負帯電制御剤				2	1.5	0.8
トナー特性						
d_v (μm)	7.1	7.0	7.1	7.2	7.1	7.3
d_v/d_p	1.22	1.21	1.21	1.27	1.24	1.30
形状 (r_1/r_s)	1.1	1.2	1.1	1.2	1.2	1.3
熔融粘度 ($\text{Pa} \cdot \text{s}$)	7500	7400	6800	9200	8400	7700
THF不溶分量 (%)	21	19	23	38	28	31
体積固有抵抗 ($\log(\Omega \cdot \text{cm})$)	11.5	11.6	11.7	11.7	11.3	11.6
官能基量比 (P:Q)	0.21:1	0.13:1	0.09:1	—	—	—
L/L帯電 ($\mu\text{C/g}$)	-23	-23	-24	-40	-28	-66
N/N帯電 ($\mu\text{C/g}$)	-22	-22	-23	-22	-22	-23
H/H帯電 ($\mu\text{C/g}$)	-21	-20	-21	-18	-19	-20
着色剤分散性 2 (個)	2	0	1	96	69	78
画質評価						
色調 L*	56.9	75.5	87.3	67.2	81.4	87.8
a*	78.1	-30.2	-17.9	47.4	-22.5	-13.3
b*	-34.4	-30.4	77.6	-23.3	-20.3	48.2
印字濃度	1.55	1.54	1.49	1.37	1.37	1.38
カブリ	0.1	0.3	0.5	4.2	5.6	3.3
定着温度 (°C)	130	135	130	145	145	140
オフセット発生温度 (°C)	220	220	220	220	220	220

[0098] From Tables 2 and 3. The polycondensation of the polyhydric alcohol (A2) containing the polyvalent-carboxylic-acid compound (A1) which contains an amino group or its salt as right electrification control resin and/or an amino group, or its salt is carried out. The toner of the comparative examples 1-6 which carry out the polycondensation of the polyhydric alcohol (J2) containing the polyvalent-carboxylic-acid compound (J1) which contains a sulfonic group or its salt as the becoming polyester resin and negative electrification control resin and/or a sulfonic group, or its salt and which do not carry out polyester resin content, Electrification quantity is understood that pigment dispersibility and a color tone are bad, printing density's are low, and there are in fogging. [many] On the other hand, the toner of this invention has high environmental stability, pigment dispersibility and a color tone are good, printing density is high, and it turns out that fogging can also be lessened.

[0099]

[Effect of the Invention] Also in the fixing apparatus which combined the heat-resistant film and thermal head in which power saving and a quick start are possible, the toner of this invention has a large interval of fixing starting temperature and offset starting temperature, and the good low-temperature-fixation characteristic, the surface smoothness of a high fixed image, and high-temperature-preservation nature are shown. Since it excels in the stability of electrification quantity and excels in the dispersibility of colorant, the reproducibility of a color picture is high, a clear picture can be acquired, there is little fogging, and printing density can also be made high, and also it excels also in durable printing nature.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]This invention relates to a toner and a manufacturing method for the same. In detail, it is related with a clear color tone, stable electrification, a toner that has the outstanding transfer nature, and a manufacturing method for the same irrespective of an one-ingredient method and a two-ingredient method.

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PRIOR ART

[Description of the Prior Art]In recent years, the full color electrophotography device, especially the digitized full color electrophotography device attract attention, and it is being widely developed by the commercial scene with expansion of automation. As a toner for electro photography (it may only be hereafter called a "toner".) used for an electrophotography device, The particles which add and knead colorant, a charge controlling agent, etc. to binding resin, and are subsequently mainly manufactured by grinding and what is called pulverizing method classified further (pulverizing method particles), Or the particles (the polymerizing method particles) manufactured by polymerizing by methods, such as suspension polymerization, an emulsion polymerization, and a distributed polymerization, and making mixtures, such as a polymerization nature monomer, colorant, and a charge controlling agent, meet if needed are mainly used. The toners used for it differ and it is classified into the negative triboelectric charging toner and the positive triboelectric charging toner according to the electrifying system of a photo conductor.

[0003]Colorization progresses also in a xerography these days and the color toner corresponding to a color image forming device is called for. Equipping a color image forming device with two or more image formation parts, forming the toner image from which a color differs by each image formation part, respectively, and color-printing by putting the color toner image of yellow, magenta, cyanogen, black, etc. on the same recording medium one by one, and transferring it is known. Even though it uses any, such as pulverized toner and polymerization toner, the following [use / as color toner] is demanded.

[0004](1) Transparency of a toner is high in order to carry out a multicolor pile.

(2) In order to make a color reproduce, a spectrum reflection property be excellent.

(3) Control electrification of a toner positive or negative precisely.

(4) Low temperature fixation be possible.

(5) Manufacture of color toner be easy.

[0005]Various examination is performed in order to meet these demands. For example, in JP,61-149969,A. The toner composition which grinds the paints processed with the additive agent for electrification strengthening which mixed and prepared additive agents for electrification strengthening, such as a homogeneous polymer of an amine content monomer, and paints by the roll mill among halogenated hydrocarbon, such as chloroform, after melting mixing with a resin particle is indicated. In JP,62-119549,A, binding resin is dissolved in a solvent, colorant and a charge controlling agent are added into this solution, a solvent is removed with a freeze drying method after stirring mixing, and the toner production method which carries out grinding classification of the toner subsequently obtained is indicated. In JP,03-155568,A, binding resin and at least one of a color and the paints. The mix of the organic solvent is carried out, the masterbatch of a color or paints is manufactured, and the manufacturing method of the toner which accepts binding resin and necessity further, kneads by mixing other additive agents and carries out grinding classification of this masterbatch is indicated. To JP,4-242752,A, paints are heated in binding resin, Melting and kneading of the pitch powder type paints produced by carrying out application-of-pressure kneading are carried out with binding resin, and the manufacturing method of the color toner to distribute and the color toner which the number rate

of a paints particle of 0.3 micrometers or more is distributing at 0.1% or less with the circular nominal diameter which exists in binding resin are indicated.

[0006]However, it is fairly difficult to satisfy the demand of the versatility of said color toner simultaneously also by these methods. Especially the thing for which it has the stable electrostatic property, and it excels in transparency and the good color toner of a spectrum reflection property is manufactured was difficult.

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EFFECT OF THE INVENTION

[Effect of the Invention]Also in the fixing apparatus which combined the heat-resistant film and thermal head in which power saving and a quick start are possible, the toner of this invention has a large interval of fixing starting temperature and offset starting temperature, and the good low-temperature-fixation characteristic, the surface smoothness of a high fixed image, and high-temperature-preservation nature are shown. Since it excels in the stability of electrification quantity and excels in the dispersibility of colorant, the reproducibility of a color picture is high, a clear picture can be acquired, there is little fogging, and printing density can also be made high, and also it excels also in durable printing nature.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]In electro photography, the purpose of this invention can acquire a clear picture and there is in providing a toner with which electrostatic property does not change even if placed under different environment, and a manufacturing method for the same. When it applies to especially color toner, it excels in the spectral characteristics, such as transparency required for reappearance of the clear color tone of a color picture, and there is little fogging, and printing density can be made high, and also it is in providing a toner excellent also in durable printing nature, and a manufacturing method for the same. As a result of repeating research wholeheartedly to achieve the above objects, this invention person is using right electrification control resin and negative electrification control resin which consist of specific polyester resin, finds out that said purpose can be attained, and came to complete this invention.

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MEANS

[Means for Solving the Problem]According to this invention, (1) binding resin, colorant, right electrification control resin, and negative electrification control resin are contained in this way, It is polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) in which this right electrification control resin contains an amino group or its salt and/or an amino group, or its salt, A toner which is polyester resin which carries out the polycondensation of the polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) in which this negative electrification control resin contains a sulfonic group or its salt and/or a sulfonic group, or its salt, (2) Right electrification control resin 100 weight section which consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing an amino group or its salt and/or an amino group, or its salt, A process of mixing ten to colorant 200 weight section, and zero to organic solvent 100 weight section which may dissolve this right electrification control resin, and obtaining a right electrification control resin composition, And negative electrification control resin 100 weight section which consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group or its salt and/or a sulfonic group, or its salt and ten to colorant 200 weight section, Zero to organic solvent 100 weight section which may dissolve this negative electrification control resin is mixed, and manufacturing method ** of a toner having the process of obtaining a negative electrification control resin composition is provided.

[0009]

[Embodiment of the Invention]The toner of this invention contains binding resin, colorant, right electrification control resin, and negative electrification control resin at least. The right electrification control resin contained in the toner of this invention consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing the polyvalent-carboxylic-acid compound (A1) containing an amino group or its salt and/or an amino group, or its salt. An amino group or its salt is not contained in polyhydric alcohol (A2) containing the polyvalent-carboxylic-acid compound (A1) containing the amino group mentioned later or its salt and/or an amino group, or its salt, and the other polyvalent-carboxylic-acid compounds or polyhydric alcohol which can carry out copolycondensation.

[0010]As a polyvalent-carboxylic-acid compound (A1) containing the amino group which constitutes polyester resin as right electrification control resin, or its salt, Aminoterephthalic acid, 5-aminoisophthalic acid, 5-aminoisophthalic acid methyl ester, 4-aminophthalic acid, 4-aminophthalic acid anhydride, 4-aminonaphthalene 2,7-dicarboxylic acid, 5 - [4-aminophenoxy] Aromatic polyvalent carboxylic acid, such as isophthalic acid; 5-amino hexahydro isophthalic acid, 5-amino hexahydro isophthalic acid methyl ester, 4-aminohexahydrophthalic acid, 4-amino hexahydrophthalic anhydride; alicyclic-polycarboxylic-acid [, such as 5-amino tetrahydro isophthalic acid, 5-amino tetrahydro isophthalic acid methyl ester, 4-amino tetrahydrophthalic acid, and 4-amino tetrahydrophthalic anhydride,]; etc. are mentioned. As polyhydric alcohol (A2) containing an amino group or its salt, Chain aliphatic-polyhydric-alcohol;2-amino-4-hydroxymethylbenzyl alcohol, such as 2-amino-2-methyl-1,3-propanediol and diethanolamine, 2-

amino-3-hydroxymethylbenzyl alcohol, 4-amino-2-hydroxymethylbenzyl alcohol, Aromatic polyhydric alcohol, such as 5-amino-3-hydroxymethylbenzyl alcohol; alicycle fellows polyhydric alcohol; such as 2,4-bis(hydroxyethyl)-1-aminocyclohexane, and those ammonium salt are mentioned.

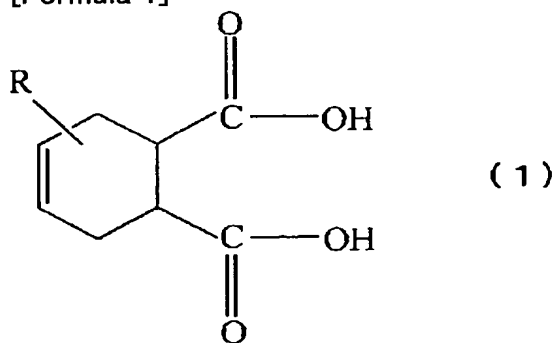
[0011]The polyester resin which has ammonium salt, Copolycondensation of the polyhydric alcohol (A2) which has the polyvalent-carboxylic-acid compound (A1) and/or ammonium salt which have the ammonium salt like the above may be carried out, and, After carrying out copolycondensation of the polyhydric alcohol (A2) which has the polyvalent-carboxylic-acid compound (A1) and/or amino group which have an amino group, what was ammonium-salt-ized may be used. In polyester resin as right electrification control resin contained in the toner of this invention, The quantity of polyhydric alcohol (A2) containing the polyvalent-carboxylic-acid compound (A1) containing an amino group or its salt and/or an amino group, or its salt, the total monomer (sum total of all the carboxylic acid components and all the alcohol components) which constitutes polyester resin — usually — 0.2-30-mol % — it is 0.5-10-mol % preferably. By containing this polyvalent-carboxylic-acid compound (A1) and/or polyhydric alcohol (A2) as a polycondensation ingredient, the dispersibility of the paints in a toner can improve and the electrostatic property of a toner can be controlled.

[0012]As for polyester resin as right electrification control resin, it is preferred that copolycondensation of the cyclic divalent-carboxylic-acid compound (B) is carried out further. As a cyclic divalent-carboxylic-acid compound (B), an aromatic divalent-carboxylic-acid compound and an alicycle fellows divalent-carboxylic-acid compound are mentioned, and an alicycle fellows divalent-carboxylic-acid compound is preferred. As an aromatic divalent-carboxylic-acid compound, derivatives, such as 1,5-naphthalic acid, 2,6-naphthalic acid, diphenic acid, terephthalic acid, isophthalic acid, phthalic acid, these alkylation objects and these acid anhydrides, a halogenide, ester, and amide, are mentioned.

[0013]An alicycle fellows divalent-carboxylic-acid compound is a compound in which fat ring structure, two carboxyl groups, or a carboxylic acid derivative group exists in molecular structure. As fat ring structure, the thing of many rings, such as monocycle; norbornane rings, such as a cyclopentane ring, a cyclohexane ring, a cycloheptane ring, and a cyclohexene ring, and a norbornene ring, is mentioned. As a suitable alicycle fellows divalent-carboxylic-acid compound, a carboxyl group or a carboxylic acid derivative group (an amide group, an ester group, and an acid anhydride group.) The alicycle fellows divalent-carboxylic-acid compound which acid halide combines with each two carbon atom which constitutes alicycle; an alkyl group like the alicycle fellows divalent carboxylic acid expressed with the general formula (1) or (2) or those anhydrides has combined with alicycle as a substituent. [especially] As an alkyl group, a methyl group, an ethyl group, a propyl group, an isopropyl group, etc. are preferably mentioned to the thing of 1-8 carbon numbers, and a concrete target.

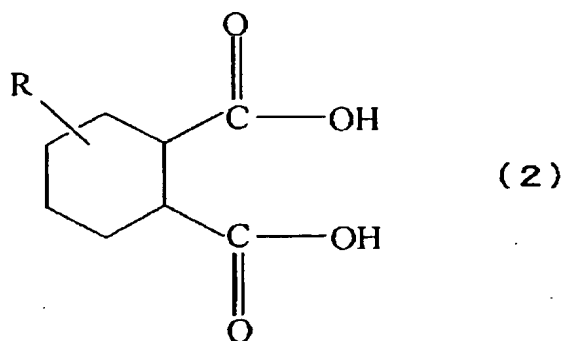
[0014]

[Formula 1]



[0015]

[Formula 2]



[0016]R in a formula (1) or (2) is an alkyl group.

[0017]An alicycle fellows divalent-carboxylic-acid compound preferably used for polyester resin as right electrification control resin makes a diene compound and; maleic anhydrides, such as butadiene, isoprene, piperylene, and a cyclopentadiene, react, and is obtained by hydrogenating if needed etc., for example. As an example of an alicycle fellows divalent-carboxylic-acid compound, Tetrahydro terephthalic acid, tetrahydro isophthalic acid, tetrahydrophthalic acid; Hexahydro terephthalic acid, Hexahydro isophthalic acid, hexahydrophthalic acid; 3-alkyl tetrahydro terephthalic acid, 4-alkyl tetrahydro terephthalic acid, 3-alkyl tetrahydro isophthalic acid, 4-alkyl tetrahydro isophthalic acid, 3-alkyl tetrahydrophthalic acid, 4-alkyl tetrahydrophthalic acid; 3-alkyl hexahydro terephthalic acid, 4-alkyl hexahydro terephthalic acid, 3-alkyl hexahydro isophthalic acid, 4-alkyl hexahydro isophthalic acid, 3-alkyl hexahydrophthalic acid, 4-alkyl hexahydrophthalic acid; 3,6- and methylene-tetrahydro terephthalic acid, 3,6- and methylene-tetrahydro isophthalic acid, 3,6-, methylene-tetrahydrophthalic acid; 3,6- and methylene-hexahydro terephthalic acid, 3,6- and methylene-hexahydro isophthalic acid, 3,6-, and methylene-hexahydrophthalic acid;

[0018]2-alkyl 3,6- and methylene-tetrahydro terephthalic acid, 3-alkyl 3,6- and methylene-tetrahydro terephthalic acid, 2-alkyl 3,6- and methylene-tetrahydro isophthalic acid, 3-alkyl 3,6- and methylene-tetrahydro isophthalic acid, 2-alkyl 3,6- and methylene-tetrahydrophthalic acid, and 3-alkyl 3,6-, methylene-tetrahydrophthalic acid; 2-alkyl 3,6-, and methylene-hexahydro terephthalic acid, 3-alkyl 3,6- and methylene-hexahydro terephthalic acid; 2-alkyl 3,6- and methylene-hexahydro isophthalic acid, 3-alkyl 3,6- and methylene-hexahydro isophthalic acid, and 2-alkyl 3,6- and methylene-hexahydrophthalic acid, and 3-alkyl 3,6- and methylene-hexahydrophthalic acid; are mentioned.

[0019]As an example of a derivative of an alicycle fellows divalent-carboxylic-acid compound, A tetrahydrophthalic anhydride, a hexahydrophthalic anhydride, 3-alkyl tetrahydrophthalic anhydride, Acid anhydrides, such as 3-alkyl hexahydrophthalic anhydride, 4-alkyl tetrahydrophthalic anhydride, and 4-alkyl hexahydrophthalic anhydride; a halogenide, ester, amide, etc. are mentioned. These are independent, respectively or can be used combining two or more sorts. Also in these, 3-alkyl tetrahydrophthalic acid, 3-alkyl hexahydrophthalic acid, Since a toner which is excellent in the dispersibility of colorant is obtained when the melting characteristic becomes high and 4-alkyl tetrahydrophthalic acid, 4-alkyl hexahydrophthalic acid, and these anhydrides use this polyester resin for a toner, it is desirable. As for quantity of a cyclic divalent-carboxylic-acid compound (B), it is preferred especially that it is [80 - 100 mol] % usual [of all the polyvalent carboxylic acid components which constitute polyester resin], 70 - 100-mol%. If there are few these rates, sufficient preservability of a toner may not be acquired.

[0020]As carboxylic acid components which constitute polyester resin as right electrification control resin, copolycondensation of a chain divalent-carboxylic-acid compound (D) and the carboxylic acid compound (F) more than trivalent may be carried out if needed. As a chain divalent-carboxylic-acid compound (D) in which copolycondensation is possible, succinic acid, adipic acid, azelaic acid, sebacic acid, dodecane dicarboxylic acid, fumaric acid, maleic acid, itaconic acid, etc. are mentioned. As a polyvalent-carboxylic-acid compound (F) more than trivalent, trimellitic acid, pyromellitic acid, trimesic acid, etc. are mentioned. Less than 30 mol % of all the carboxylic acid components of a rate of a chain divalent-carboxylic-acid compound (D)

is preferred. When this rate becomes large, glass transition temperature and melt viscosity become low, the blocking resistance of a toner may fall or hot offset may occur. Less than 5 mol % of all the carboxylic acid components of a rate of a polyvalent-carboxylic-acid compound (F) more than trivalent is preferred. Since weight average molecular weight of polyester resin will become high if this rate becomes large, melt viscosity of a toner may become high and the fixability of a toner may worsen.

[0021]As for polyester resin as right electrification control resin contained in a toner of this invention, it is preferred that copolycondensation of the cyclic dihydric alcohol (C) is carried out further. As cyclic dihydric alcohol (C), aromatic dihydric alcohol and alicycle fellows dihydric alcohol are mentioned, and alicycle fellows dihydric alcohol is preferred. As aromatic dihydric alcohol, PARAKI silylene glycol, meta key silylene glycol, An ethyleneoxide addition of Alt key silylene glycol and 1,4-phenyleneglycol, an ethyleneoxide addition of bisphenol A, a propylene oxide addition, etc. are mentioned. As alicycle fellows dihydric alcohol, it is 2,2-bis(4-hydroxycyclohexyl)-propane (.). Namely, hydrogenation bisphenol A, 1,4-bis(hydroxymethyl)cyclohexane, 1,3-bis(hydroxymethyl)cyclohexane, 1,2-bis(hydroxymethyl)cyclohexane, 2,2,4,4-tetramethyl 1,3-cyclohexanediol, An ethyleneoxide addition of 1,4-cyclohexanediol and hydrogenation bisphenol A and a propylene oxide addition, tricyclodecane diol, tricyclodecane dimethanol, dicyclohexyl 4,4'-diol, etc. are mentioned. Bis(hydroxycyclohexyl)-alkanes, such as hydrogenation bisphenol A, are [among these] preferred. Quantity of cyclic dihydric alcohol (C) is preferred in their being 2 – 60-mol% of all the polyhydric alcohol components which constitute polyester resin, and still more preferred in their being 3 – 50-mol %. If glass transition temperature and melt viscosity become low, blocking resistance may fall, or hot offset may occur, when there is too little quantity of cyclic dihydric alcohol (C), and quantity of alicycle fellows dihydric alcohol increases too much conversely, Melt viscosity may become high and fixability may fall.

[0022]As other alcohol components which constitute polyester resin as right electrification control resin, it is preferred that copolycondensation of the chain dihydric alcohol (E) is carried out further. Copolycondensation of the alcohol (G) more than trivalent may be carried out. As chain dihydric alcohol (E), ethylene glycol, a diethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, diethylene glycol, polyethylene glycols, Straight-chain-shape aliphatic series glycols, such as polytetramethylene glycol; Propylene glycol, Branched-chain aliphatic series glycols, such as dipropylene glycol, polypropylene glycol, neopentyl glycol, 2,2,4-trimethyl 1,3-pentanediol, and 2-ethyl-2-butyl-1,3-propanediol, etc. are mentioned. In these, straight-chain-shape aliphatic series glycol is preferred, and especially ethylene glycol is preferred also in it. Quantity of chain dihydric alcohol (E) is preferred in their being 40 – 98-mol% of all the polyhydric alcohol components which constitute polyester resin, and still more preferred in their being 50 – 97-mol %. When melt viscosity may become high, fixability may fall, when there is too little quantity of chain dihydric alcohol (E), and quantity of chain dihydric alcohol increases too much conversely, glass transition temperature and melt viscosity become low, blocking resistance may fall or hot offset may occur. As alcohol (G) more than trivalent, trimethylolpropane, glycerin, pentaerythritol, dipentaerythritol, trimethylolethane, cyclohexane triol, tris(hydroxymethyl) cyclohexane, etc. are mentioned. Less than 5 mol % of all the alcohol components of a rate of alcohol (G) more than trivalent is preferred. Since weight average molecular weight of polyester resin will become high if this rate becomes large, melt viscosity of a toner may become high and the fixability of a toner may worsen.

[0023]A molecular weight of polyester resin as right electrification control resin contained in a toner of this invention, When it measures with gel permeation chromatography (GPC), by polystyrene conversion. a number average molecular weight — 1,500–20,000 — it is 2,000–10,000 preferably — weight average molecular weight — desirable — 5,000–300,000 — it is 7,000–100,000 preferably. When a molecular weight is in this range, a toner excellent in low temperature fixability and hot offset tolerance can be obtained. When a number average molecular weight and weight average molecular weight are smaller than a mentioned range, cohesive force of resin may decline, preservability may get worse, when conversely large, productivity may fall and the fixability of a toner may get worse. 40–90 ** of glass transition

temperature of electrification control resin is 50–80 ** especially preferably preferably. The preservability of a toner will be improved if glass transition temperature is a mentioned range. [0024]A hydroxyl value is usually 1 – 100 mgKOH/g, and polyester resin as right electrification control resin is a thing of 5 – 80 mgKOH/g preferably. When a hydroxyl value is small, fixability may worsen, big unevenness may arise on the surface of a picture, and smooth nature may fall. Conversely, when large, hot offset generating temperature becomes low, hydrophilic nature becomes high further, and it is in a tendency for electrification quantity to change with environmental variations easily. As for electrification control resin, in order to lessen influence of moisture in a high-humidity/temperature environment, it is preferred to lessen an aromatic ring more.

[0025]Polyester resin as right electrification control resin contained in a toner of this invention can be manufactured by a publicly known method, i.e., a polycondensation method. A total of a hydroxyl value of the inside of a total monomer which totaled a polyvalent carboxylic acid component and a polyhydric alcohol component in carrying out the polycondensation of a polyvalent carboxylic acid component and the polyhydric alcohol component, and an alcoholic reactivity group [X] A total of acid value of said carboxylic acid sexual response nature group [Y] Since also performing a twist on conditions which do not become small can make a molecular weight of polyester high and it can make a hydroxyl value high, it is preferred. A total of a hydroxyl value of an alcoholic reactivity group [X]A total of acid value of a carboxylic acid sexual response nature group [Y]Rate[X]/1.00 or more equivalent ratio of [Y] is preferred, 1.01–1.5 are more preferred, and especially the range of 1.03–1.3 is preferred. The alcoholic reactivity group refers to an alcoholic functional group in which an ester bond is made to form here, and hydroxyl etc. are usually mentioned. The carboxylic acid sexual response nature group refers to a functional group of carboxylic acid nature in which an ester bond is made to form, and a carboxyl group or a carboxylic acid derivative group is usually mentioned.

[0026]As for a polycondensation reaction, it is preferred that it is carried out at 150–280 **, and reaction temperature of 100–300 ** carries out especially under existence of inactive gas preferably for example. An organic solvent of nonaqueous solubility which carries out azeotropy to water, such as toluene and xylene, may be used if needed. A polycondensation reaction may be performed under decompression (usually 0.1 – 500mmHg, preferably 0.5 – 200mmHg, more preferably 1 – 50mmHg). An esterification catalyst is usually used for this polycondensation reaction. As an esterification catalyst, for example Para toluenesulfonic acid, sulfuric acid, Broensted acid, such as phosphoric acid; Calcium acetate, zinc acetate, manganese acetate, zinc stearate; — acetylacetonato [of iron or zinc]; — metal alkoxide; — alkyl tin oxide. Organic metallic compounds, such as dialkyl tin oxide and an organic titanium compound : Tin oxide, Metallic oxides, such as antimony oxide, titanium oxide, and vanadium oxide: Titanium alkoxide, heteropoly acid, or iron acetylacetonato is preferred at a point which can carry out polymers quantification of the polyester obtained by mentioning heteropoly acid etc.

[0027]In order to obtain polyester resin as right electrification control resin contained in a toner of this invention, the above-mentioned carboxylic acid compound and alcohol may be prepared and put in block, and may be made to react by desired composition ratio, and a following method can also be used in order to adjust a molecular weight. Namely, a cyclic divalent-carboxylic-acid compound (B) and cyclic dihydric alcohol (C) preferably, Carry out the polycondensation of a cyclic divalent-carboxylic-acid compound (B), cyclic dihydric alcohol (C) and a chain divalent-carboxylic-acid compound (D), and/or the chain dihydric alcohol (E), obtain a precursor, and it ranks second, The polycondensation of polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing this precursor, an amino group, or its salt and/or an amino group, or its salt and a polyvalent-carboxylic-acid compound (H), and/or polyhydric alcohol (I) is carried out.

[0028]a time of measuring a precursor with gel permeation chromatography (GPC) — polystyrene conversion — the number average molecular weight — 1,500–5,000 — it is 2,000–4,000 preferably. The dispersibility of resin becomes high when a molecular weight is in this range. Not less than 40 ** of glass transition temperature of a precursor is 50–80 ** especially preferably preferably. The preservability of a toner will be improved if glass transition

temperature is not less than 40 **.

[0029]A polyvalent-carboxylic-acid compound (H) which carries out copolycondensation to polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing a precursor and an amino group, or its salt and/or an amino group, or its salt, Especially, it is not restricted but an aromatic divalent-carboxylic-acid compound which was mentioned above and a cyclic divalent-carboxylic-acid compound (B) like an alicycle fellows dicarboxylic acid compound, a chain divalent-carboxylic-acid compound (D), a carboxylic acid compound (F) more than trivalent, etc. can be mentioned. A cyclic divalent-carboxylic-acid compound which a carboxyl group or a carboxylic acid derivative group combined with each two carbon atom like terephthalic acid, tetrahydro terephthalic acid, and hexahydro terephthalic acid which constitutes a ring, and which does not adjoin each other also in these is preferred. Polyhydric alcohol (I) which carries out copolycondensation to polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing a precursor and an amino group, or its salt and/or an amino group, or its salt, Especially, it is not restricted but cyclic dihydric alcohol (C) like aromatic dihydric alcohol which was mentioned above, or alicycle fellows dihydric alcohol, chain dihydric alcohol (E), alcohol (G) more than trivalent, etc. can be mentioned. The total quantity of a polyvalent-carboxylic-acid compound (H) used for copolycondensation with a precursor or polyhydric alcohol (I) is 20 - 40 weight section especially preferably ten to 50 weight section preferably to precursor 100 weight section. When quantity of this polyvalent-carboxylic-acid compound or polyhydric alcohol is in a mentioned range, since polymers quantification can be carried out without spoiling the melting characteristic, it is desirable.

[0030]Negative electrification control resin contained in a toner of this invention consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group or its salt and/or a sulfonic group, or its salt. This negative electrification control resin polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing an amino group which constitutes right electrification control resin mentioned above, or its salt and/or an amino group, or its salt, It can obtain by transposing to polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group or its salt and/or a sulfonic group, or its salt, and carrying out a polycondensation to it. Therefore, a cyclic divalent-carboxylic-acid compound (B) which can carry out copolycondensation, What was mentioned above can be used for a carboxylic acid compound (F) more than cyclic dihydric alcohol (C), a chain divalent-carboxylic-acid compound (D), chain dihydric alcohol (E), and trivalent, and alcohol (G) more than trivalent. An above-mentioned method can also make the manufacturing method the same.

[0031]As a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group which constitutes polyester resin as negative electrification control resin, or its salt, Sulfoterephthalic acid, 5-sulfoisophtharate, 5-sulfoisophtharate methyl ester, 4-sulfophthalic acid, 4-sulfophthalic acid anhydride, 4-sulfonaphthalene-2,7-dicarboxylic acid, 5 - [4-sulfophenoxy] Isophthalic acid; 5-sulfo hexahydro isophthalic acid, 5-sulfo hexahydro isophthalic acid methyl ester, Aromatic multivalent sulfonic acid; 5-sulfo tetrahydro isophthalic acid, such as 4-sulfo hexahydrophthalic acid and 4-sulfo hexahydrophthalic anhydride, Alicycle fellows multivalent sulfonic acid [, such as 5-sulfo tetrahydro isophthalic acid methyl ester, 4-sulfo tetrahydrophthalic acid, and 4-sulfo tetrahydrophthalic anhydride,], those salts, etc. are mentioned. As a sulfonate, salts, such as ammonium, Li, Na, K, Mg, Ca, Cu, and Fe, are mentioned. In particular, K salt or Na salt is preferred. As polyhydric alcohol (J2) containing a sulfonic group or its salt, 2,3-bis(hydroxymethyl)benzenesulfonic acid, 3,5-bis(hydroxymethyl)benzenesulfonic acid, 3,4-bis(hydroxymethyl)benzenesulfonic acid, 2,5-bis(hydroxymethyl)benzenesulfonic acid, those salts, etc. are mentioned. As a sulfonate, salts, such as ammonium, Li, Na, K, Mg, Ca, Cu, and Fe, are mentioned. In particular, K salt or Na salt is preferred.

[0032]In polyester resin as negative electrification control resin contained in a toner of this invention, Quantity of polyhydric alcohol (J2) containing a polyvalent-carboxylic-acid compound (J1) containing a sulfonic group or its salt and/or a sulfonic group, or its salt, a total monomer (sum total of all the carboxylic acid components and all the alcohol components) which constitutes polyester resin — usually — 0.2-30-mol % — it is 0.5-10-mol % preferably. By

containing this polyvalent-carboxylic-acid compound (J1) and/or polyhydric alcohol (J2) as a polycondensation ingredient, the dispersibility of paints in a toner can improve and the electrostatic property of a toner can be controlled.

[0033] Here, in a toner of this invention, although right electrification control resin and negative electrification control resin are used together, the rates differ by whether a toner is made into positive triboelectric charging, or it is considered as negative triboelectric charging. An amino group which brings about positive triboelectric charging in right electrification control resin in obtaining a positive triboelectric charging toner, or the number of mol equivalents of the salt. (it is hereafter called a "right functional group amount".) — content in a toner of each electrification control resin is adjusted so that it may increase more than the number of mol equivalents of a sulfonic group which brings about negative triboelectric charging in negative electrification control resin, or its salt (henceforth "a negative functional group amount"). In obtaining a negative triboelectric charging toner, a negative functional group amount adjusts a using rate of each electrification control resin so that it may increase more than a right functional group amount.

[0034] The right functional group amount P a product of weight % of an amino group which brings about positive triboelectric charging in "right electrification control resin, or its salt, and a right electrification control resin amount in a toner specifically, It is computable as what $\frac{P}{Q}$ with a molecular weight of a structural unit which has an amino group which brings about positive triboelectric charging in right electrification control resin, or its salt. The negative functional group amount Q "a product of weight % of a sulfonic group which brings about negative triboelectric charging in negative electrification control resin, or its salt, and a negative electrification control resin amount in a toner, It is computable as what $\frac{Q}{P}$ with a molecular weight of a structural unit which has a sulfonic group which brings about negative triboelectric charging in negative electrification control resin, or its salt. a case of a positive triboelectric charging toner — a ratio (P:Q) of the right functional group amount P and the negative functional group amount Q — usually — 1:0.005 to 1:0.9 — desirable — 1:0.01 to 1:0.8 — it is determined that it is more preferably set to 1:0.05 to 1:0.7 by rate of each electrification control resin. a case of a negative triboelectric charging toner — a ratio (Q :P) of the negative functional group amount Q and the right functional group amount P — usually — 1:0.005 to 1:0.9 — desirable — 1:0.01 to 1:0.8 — it is determined that it is more preferably set to 1:0.05 to 1:0.7 by rate of each electrification control resin. In this functional group amount ratio, when one ratio was too small and continuous printing is carried out, fault of that an electrification controllability becomes high too much and printing endurance and printing density fall, a toner dispersing may be produced. On the contrary, when one ratio is too large, electrostatic property may become insufficient and problems, such as fogging, may be produced.

[0035] In this invention, by using together negative electrification control resin and right electrification control resin, By using together by said functional group ratio desirably, electrostatic property seldom changes also in which environment under low-humidity/temperature and high-humidity/temperature, but further, even if it performs continuous printing, a toner with which deterioration of image quality and generating of fogging are controlled can be obtained.

[0036] A toner of this invention is the sum total, and is usually carrying out 0.03–10 weight-section content of polyester resin as right electrification control resin, and the polyester resin as negative electrification control resin preferably 0.01 to 20 weight section to the binding resin 100 below-mentioned weight section. If there is little quantity of polyester resin, electrification controlling performance will not appear, but if too large, variation width of electrification quantity by an environmental variation will become large easily.

[0037] Even if a toner of this invention does not use other charge controlling agents together other than polyester resin mentioned above, it shows practically sufficient electrifying characteristic. However, the conventional charge controlling agent may be used together for the purpose, such as fine adjustment. It is possible to use a charge controlling agent of various kinds of positive triboelectric charging or negative triboelectric charging as other charge controlling agents. For example, a metal complex of an organic compound which has a carboxyl group or a

nitrogen-containing basis, metallized dye, Nigrosine, etc. are mentioned. More specifically SUPIRON black TRH (made by the Hodogaya chemical industry company), T-77 (made by the Hodogaya chemical industry company), BONTORON S-34 (made by an Orient chemical industry company), BONTORON E-84 (made by an Orient chemical industry company), BONTORON N-01 (made by an Orient chemical industry company), other electrification control resin, such as charge controlling agents, such as copy blue PR (made by Clariant, LTD.), and/or the 4th class ammonium (salt) group content (meta-) acrylate system copolymer, and a sulfonic acid (salt) group content acrylate system copolymer, can be mentioned.

[0038]A polymer currently used for usual can be used for binding resin contained in this invention toner as binding resin of a toner. Specifically Polystyrene, styrene (meta) acrylate copolymerization resin, Polyester resin other than the above, polyurethane, an epoxy resin, polyolefine, A core hydrogenation thing of polyamide, polysulfone, polish anoa reel ether, acrylate (meta) resin, norbornene system resin, and styrene resin, a core hydrogenation thing of styrene isoprene styrene block polymer, etc. are mentioned.

[0039]As colorant contained in a toner of this invention, there are black colorant, a yellow coloring agent, a magenta coloring agent, cyanogen colorant, etc. As black colorant, magnetic particle [, such as carbon black, the dyes-and-pigments; cobalt of the Nigrosine base, nickel, a tri-iron tetraoxide, iron oxide manganese, iron oxide zinc and iron oxide nickel,]; etc. can be mentioned. When using carbon black, since good image quality will be obtained and safety to environment of a toner will also increase if primary particle diameter uses what is 20-40 nm, it is desirable. As a yellow coloring agent, compounds, such as azo pigment and condensed polycyclic pigment, are used. Specifically, the C.I. pigment yellow 3, 12, 13, 14, 15, 17, 62, 65, 73, 83, 90, 93, 97, 120, 138, 155, and 180 and 181 grades are mentioned. As a magenta coloring agent, compounds, such as azo pigment and condensed polycyclic pigment, are used. Specifically The C.I. pigment red 48, 57, 58, 60, 63, 64, 68, 81, 83, 87, 88, 89, 90, 112, 114, 122, 123, 144, 146, 149, 163, 170, 184, 185, 187, 202, 206, 207, and 209, 251, the C.I. pigment violet 19, etc. are mentioned. As cyanogen colorant, a copper-phthalocyanine compound and its derivative, an anthraquinone compound, etc. can be used. Specifically, the C.I. pigment blues 2, 3, 6, 15, 15:1, 15:2, 15:3, 15:4, 16, and 17 and 60 grades are mentioned. Quantity of these colorant is usually one to 20 weight section preferably 0.1 to 50 weight section to binding resin 100 weight section.

[0040]A toner of this invention may contain a release agent from viewpoints of an improvement of low temperature fixability, prevention from filming, etc. As a release agent, for example Low molecular weight polyethylene, low molecular weight polypropylene, Polyolefine waxes, such as low-molecular-weight polybutylene; Candelilla, Vegetable system natural wax, such as carnauba, rice, and haze wax; Paraffin, Synthetic waxes, such as petroleum system wax; Fischer Tropsch waxes, such as micro crystalline and PETORO lactam; Pentaerythritol tetra Millis Tait, Polyfunctional ester compounds, such as pentaerythritol tetra palmitate and dipentaerythritol hexa Millis Tait, etc. are mentioned. These can be used combining one sort or two sorts or more.

[0041]A synthetic wax (especially the Fischer Tropsch wax), a petroleum system wax, a polyfunctional ester compound, etc. are [among these] preferred. In a DSC curve measured with a differential scanning calorimeter also in these, Endothermic peak temperature at the time of temperature up preferably 30-200 ** 50-180 **, Polyfunctional ester compounds, such as pentaerythritol ester which is in the range of 60-160 ** preferably especially, and dipentaerythritol ester in a range in which the endothermic peak temperature is 50-80 **, are preferred especially in respect of fixing-detachability balance as a toner. A molecular weight is especially 1000 or more, five or more weight sections dissolve at 25 ** to styrene 100 weight section, and, as for dipentaerythritol ester which is 10 or less mg/KOH, acid value shows higher efficacy to a fixing temperature fall. Endothermic peak temperature is the value measured by ASTM D3418-82. Quantity of the above-mentioned release agent is usually one to 15 weight section preferably 0.1 to 20 weight section to binding resin 100 weight section.

[0042]1-10 micrometers of volume average particle diameter (dv) of a toner of this invention are usually 3-8 micrometers preferably — a ratio (dv/dp) of volume average particle diameter to number average particle diameters (dp) — 1-2.0 — it is 1-1.5 preferably. It is preferred that

ranges of a value (r_l/r_s) which broke the major axis r_l of a toner by the minor axis r_s are 1–1.3. When this ratio becomes large, transfer nature which transfers a toner image on a photoconductor to transfer materials, such as paper, may fall, or since friction between toners becomes large when this toner is dedicated to a toner compartment of an image forming device, an external additive may exfoliate, and endurance may fall.

[0043]a toner of this invention — melt viscosity in 120 ** — usually — 10,000 or less Pa·s — desirable — 100–10,000 Pa·s — it is 1,000 – 8,000 Pa·s more preferably. According to the toner with such melt viscosity, high definition is realized also by printing at a high speed. Measurement of viscosity can be measured using a flow tester. 50–80 ** of softening temperature by a flow tester is usually 60–70 ** preferably, and 90–150 ** of outflow starting temperature is usually 100–130 ** preferably. When softening temperature is low, preservability may fall, and when conversely high, fixability may fall. When outflow starting temperature is low, hot offset tolerance may fall, and when conversely high, fixability may fall. 0–80 ** of glass transition temperature according [a toner of this invention] to a differential scanning calorimeter is usually 40–70 ** preferably. When glass transition temperature is low, preservability may fall, and when conversely high, fixability may fall.

[0044]A tetrahydrofuran (THF) insoluble daily dose of a toner of this invention is usually 0 to 20% preferably 0 to 50%. A fall of a gross and aggravation of transparency occur in not less than 50%. A THF insoluble daily dose can be measured by a below-mentioned method. a volume specific resistance value ($\log(\text{ohm-cm})$) according [a desirable toner used for this invention] to a dielectric loss measuring instrument — usually — 10–13 — it is a thing of 10.5–12.5 preferably. When a volume specific resistance value is small, fogging may occur, and when conversely large, toner scattering, fogging, filming, or cleaning defect may occur. As for a toner of this invention, it is preferred that there is little electrification quantity change in a high-humidity/temperature environment (H/H environment) and low-humidity/temperature environment (L/L environment) and that what is called environmental stability is high. As for variation of electrification quantity between each environment, in that case, it is preferred that it is below 5microC/g. When environmental stability is low, fogging may occur.

[0045]A toner of this invention has the preferred number of color particles with a major axis of 0.2 micrometers or more observed in an area of 100 micrometers x 100 micrometers of a toner which carried out heat melting and was made into 20 micrometers of thickness in their being 50 or less pieces, it is more preferred in their being 30 or less pieces, and is still more preferred in their being 20 or less pieces. If there are many these numbers, it will get bad to the spectral characteristics, such as transparency required for reappearance of a clear color tone of a color picture, and fogging may increase and printing density may become low. The spectral characteristic can perform solid printing with a commercial printer, and can measure the color tone with a spectrum color difference meter.

[0046]The toner of this invention can make the exterior of a toner mentioned above particles of core shell structure (it is also called capsule structure) by covering with other polymers. By intension-izing internal (core layer) low softening point material in core shell structure particles by a substance which has softening temperature higher than it, since low-temperature-izing of fixing temperature and prevention from condensation at the time of preservation can be balanced, it is desirable.

[0047]In the case of a core shell type toner, 0–80 ** of glass transition temperature of a polymer which constitutes a core layer is usually 40–60 ** preferably. When glass transition temperature is too high, fixing temperature may become high, and when too conversely low, preservability may fall. It is necessary to set up glass transition temperature of a polymer which constitutes a shell layer become higher than glass transition temperature of a polymer which constitutes a core layer as binding resin. Glass transition temperature of a polymer which constitutes a shell layer is 50–130 ** usually 80–110 ** more preferably 60–120 ** in order to raise the preservability of a toner. When lower than this, preservability may fall, and when conversely high, fixability may fall. Not less than 20 ** of differences of glass transition temperature of a polymer which constitutes a core layer, and glass transition temperature of a polymer which constitutes a shell layer are not less than 10 ** usually not less than 30 ** more

preferably. When smaller than this difference, balance of preservability and fixability may fall. [0048] Especially a wt. ratio of a core layer of a core shell type toner and a shell layer is usually use **** at 80 / 20 – 99.9/0.1, although not limited. If a rate of a shell layer is smaller than the above-mentioned rate, preservability will worsen, and conversely, if larger than the above-mentioned rate, it will become difficult to be established at low temperature.

[0049] It is desirable to restrict the amount of residual metals (ion) in a toner furthermore. When metal (ion), such as magnesium and calcium, remains in a developer especially, under a high-humidity condition, moisture absorption may be caused, the mobility of a developer may be reduced and it may have an adverse effect on image quality. What has few content in a developer of magnesium or calcium (only henceforth residual metals) can give good image quality without high printing density and fogging also under a high-humidity/temperature condition with a high speed machine which can print 30 or more sheets in 1 minute. 170 ppm or less of the amounts [150 ppm or less of] of residual metals are 120 ppm or less especially preferably more preferably. What is necessary is to dry using washing dehydrators, such as a continuous system belt filter and a siphon peeler type centrifuge, etc., to repeat and perform washing, and just to dry, for example in a drying stage of a toner production process, in order to reduce residual metals.

[0050] A toner of this invention, for example in thermoplastics used as ** binding resin ingredient, After carrying out melting mixing of colorant, right electrification control resin, negative electrification control resin, the release agent, etc., making it distribute uniformly and considering it as a constituent, A toner by grinding and classifying this constituent in a polymerization nature monomer which is pulverizing method and ** binding resin raw material to obtain Colorant, Right electrification control resin, negative electrification control resin, a release agent, etc. are dissolved or distributed, The drainage system carrier fluid inside of the body containing dispersion stabilizer is distributed after adding a polymerization initiator, Particles of binding resin obtained by the polymerizing method and ** emulsion polymerization which obtain a toner by warming to prescribed temperature, starting a polymerization, and filtering, washing, drying and drying after an end of a polymerization, distributed polymerization, etc., Particles containing colorant, right electrification control resin, and negative electrification control resin, The meeting method for obtaining a toner by filtering particles made to meet and drying, ** Hydrophilic radical content resin is used as binding resin, and after adding colorant, right electrification control resin, negative electrification control resin, etc. to it and making it dissolve in an organic solvent, it can manufacture by neutralizing this resin and drying phase inversion and after that with a phase inversion emulsification method etc. which obtain a toner. A toner obtained from a viewpoint of obtaining a toner which gives dot reproducibility good image quality also in this, by the polymerizing method is preferred.

[0051] Right electrification control resin 100 weight section which consists of polyester resin in which a manufacturing method of a toner of this invention carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing an amino group mentioned above or its salt and/or an amino group, or its salt, Ten to colorant 200 weight section and zero to organic solvent 100 weight section which may dissolve this electrification control resin are mixed, Negative electrification control resin 100 weight section which consists of polyester resin which carries out the polycondensation of the polyhydric alcohol (A2) containing a polyvalent-carboxylic-acid compound (A1) containing a process of obtaining a right electrification control resin composition, a sulfonic group mentioned above, or its salt and/or a sulfonic group, or its salt, Ten to colorant 200 weight section and zero to organic solvent 100 weight section which may dissolve this electrification control resin are mixed, and it has the process of obtaining a negative electrification control resin composition. In a manufacturing method of a toner of this invention, it is preferred to use an electrification control resin composition produced by mixing positive or negative electrification control resin 100 weight section, and 20 to colorant 150 weight section. By manufacturing a toner using an electrification control resin composition, colorant can be uniformly distributed in a toner.

[0052] If an organic solvent is used in manufacture of positive or a negative electrification control resin composition used by this invention, since electrification control resin can be dissolved or

swollen, it can mix in the state where resin is soft and colorant can be distributed uniformly, it is desirable. When not using an organic solvent, there is a thing with which resin warms and is not mixed to temperature which is a grade which becomes soft and which it is necessary to carry out and control of temperature becomes difficult. Since an organic solvent may evaporate by warming when especially the boiling point of an organic solvent is low when using an organic solvent, it is a room temperature or it is preferred to cool and to obtain positive or a negative electrification control resin composition. As for an organic solvent, since a problem of a bad smell may occur when an organic solvent remains in a toner, it is preferred to be removed in either at the time of manufacture of positive or a negative electrification control resin composition or manufacture of a toner. If quantity of an organic solvent is ten to 60 weight section and is in this range still more preferably five to 80 weight section preferably zero to 100 weight section to positive or negative electrification control resin 100 weight section, balance of dispersibility and processability is excellent. Checking a kneading state, even if an organic solvent adds the whole quantity at once at this time, it may divide into several times and may add.

[0053]When using an organic solvent, the solubility coefficient (henceforth an SP value) is $8 - 15 [\text{cal}/\text{cm}^3]^{1/2}$, and a thing of a range whose boiling point is 50–150 ** is preferred. If an SP value is smaller than $8 [\text{cal}/\text{cm}^3]^{1/2}$, polarity can become small and electrification control resin may be dissolved, If an SP value is conversely larger than $15 [\text{cal}/\text{cm}^3]^{1/2}$, polarity can become high and electrification control resin may be dissolved. On the other hand, when the boiling point is lower than 50 **, an organic solvent may evaporate with heat generated by kneading, and when conversely higher than 150 **, it may become difficult after kneading to remove an organic solvent. As an organic solvent, concretely (an SP value/boiling point) Methanol (14.5/65 **), Ethanol (10.0/78.3 **), propanol (11.9/97.2 **), A diethyl ketone (8.8/102 **), di-n-propyl ketone (8.0/144 **), Di-iso-propyl ketone (8.0/124 **), methyl-n-propyl ketone (8.3/102 **), Methyl-iso-propyl ketone (8.5/95 **), methyl-n-butyl ketone (8.5/127 **), Methyl-iso-butyl ketone (8.4/117 **), toluene (8.9/110 **), A tetrahydrofuran (9.1/65 **), methyl ethyl ketone (9.3/80 **), acetone (9.9/56 **), cyclohexanone (9.9/156 **), etc. are mentioned, and these may be used independently, or may mix and use two or more sorts. Also in this, in consideration of solubility to electrification control resin, and removal after kneading, a diethyl ketone, Methyl-n-propyl ketone, methyl-n-butyl ketone, toluene / methanol mixed solvent, toluene / ethanol mixed solvent, toluene / propanol mixed solvent, and methyl ethyl ketone / methanol mixed solvent are preferred.

[0054]Mixing can be performed using a roll, a PURASUCHI coder (made by the Brabender company), a lab PURASUTO mill (made by an Oriental energy machine company), a kneader, a 1 axis extrusion machine, a twin screw extruder, Banbury, the Bus ko kneader, etc. Since there are a bad smell and a toxic problem when using an organic solvent, a mixer of a sealing system in which an organic solvent does not leak is preferred. Since that a torque meter is installed in a mixer can manage dispersibility on a level of torque, it is preferred.

[0055]Positive or a negative electrification control resin composition used by this invention, After adding an organic solvent to this constituent and considering it as 5% of resin solution, on a glass plate, The number of color particles with a major axis of 0.2 micrometers or more observed in an unit area of 100 micrometers x 100 micrometers of a film from which a gap is obtained by applying and drying a resin solution with a doctor blade which is 30 micrometers is preferred in their being 20 or less pieces, more preferred in their being ten or less pieces, and still more preferred in their being five or less pieces. If there are many these numbers, it will get bad to the spectral characteristics, such as transparency required for reappearance of a clear color tone of a color picture, and fogging may increase and printing density may become low. The spectral characteristic performs solid printing with a commercial printer, and measures the color tone with a spectrum color difference meter. After adding an organic solvent and considering it as 5% of resin solution, a gap applies a mixed solution on a glass plate with a doctor blade which is 30 micrometers, When the number of color particles with a major axis of 0.2 micrometers or more observed in an unit area of 100 micrometers x 100 micrometers of a film produced by drying

uses positive [20 or less] or a negative electrification control resin composition, Heat melting can be carried out, it can be made 20 micrometers of thickness, and the number of color particles with a major axis of 0.2 micrometers or more observed in an area of 100 micrometers x 100 micrometers can obtain comparatively easily a toner which is 50 or less pieces.

[0056]In a manufacturing method of a toner of this invention, in order to make positive or a negative electrification control resin composition include in a toner, After carrying out melt kneading of the other additive agents etc. binding resin, this electrification control resin composition, and if needed, in pulverizing method and a suitable drainage system carrier fluid body which are ground and classified so that it may become the particle size distribution of an after-cooling request. Although the polymerizing method etc. which polymerize a polymerization nature monomer used as a raw material of binding resin, an electrification control resin composition, and a polymerization nature monomer composition that contains other additive agents if needed are mentioned, since a toner which gives dot reproducibility good image quality is obtained, manufacturing by the polymerizing method is preferred.

[0057]In a manufacturing method of a toner of this invention, said 0.1 to right electrification control resin composition 20 weight section, It is preferred to mix 0.1 to 20 weight section of a negative electrification control resin composition and polymerization nature monomer 100 weight section, to obtain a polymerization nature monomer composition, to polymerize this in a drainage system carrier fluid body, and to manufacture a toner. A rate of a right electrification control resin composition and a negative electrification control resin composition is whether a toner is made into positive triboelectric charging, or to consider it as negative triboelectric charging, and it can be suitably changed so that it may become the functional group amount ratio mentioned above.

[0058]Although a polymerization method in particular may not be limited but any of an emulsion polymerization, suspension polymerization, a distributed polymerization, and soap free polymerization may be sufficient, From a point which can make colorant able to contain uniformly and can raise electrostatic property and transfer nature, a suspension polymerization method is preferred and specifically, A polymerization nature monomer, a right electrification control resin composition, a negative electrification control resin composition, a regulator, a release agent, and a polymerization nature monomer composition that contains additive agents, such as a charge controlling agent, if needed are polymerized in a drainage system medium.

[0059]Hereafter, a manufacturing method of a core shell type toner by more desirable suspension polymerization is explained. In a drainage system carrier fluid body to contain, a dispersion stabilizing agent A polymerization nature monomer (polymerization nature monomer for cores), By making a polymerization nature monomer composition (monomer composition for cores) containing a right electrification control resin composition, a negative electrification control resin composition, and other additive agents suspended, and polymerizing using a polymerization initiator, A core particle can be manufactured, a polymerization nature monomer (polymerization nature monomer for shell) and a polymerization initiator for forming shell can be added further, and capsule toner can be obtained by polymerizing. How to add a polymerization nature monomer for shell to the system of reaction of a polymerization reaction which obtains said core particle and which was performed for accumulating, and polymerize continuously in it as a concrete method of forming shell, Or a core particle obtained by another system of reaction can be taught, and a method of adding a polymerization nature monomer for shell to this, and polymerizing gradually in it, etc. can be mentioned. It can add collectively in the system of reaction, or a monomer for shell ingredients can be added continuously or intermittently using pumps, such as a plunger pump.

[0060]As a polymerization nature monomer for cores, a monovinyl system monomer, a cross-linking monomer, a macro monomer, etc. can be mentioned. This polymerization nature monomer polymerizes and it becomes a binding resin ingredient. As a monovinyl system monomer, specifically Styrene, vinyltoluene, styrene monomer [, such as alpha-methylstyrene,]; (meta-) — acrylic acid; (meta-) — methyl acrylate. (Meta) Ethyl acrylate, acrylic acid (meta) propyl, butyl acrylate (meta), (Meta) 2-ethylhexyl acrylate, acrylic acid (meta) cyclohexyl, (Meta) A derivative of acrylic acid (meta), such as acrylic acid iso BONIRU, acrylic acid (meta) dimethylaminoethyl,

and acrylamide (meta); monoolefin system monomer [, such as ethylene, propylene, and butylene,]; etc. are mentioned. A monovinyl system monomer may be used independently or may be used combining two or more monomers. Concomitant use with styrene monomer independence, a styrene monomer, and a derivative of acrylic acid (meta), etc. are suitably used among these monovinyl system monomers.

[0061]If a cross-linking monomer and a polymer are used with a monovinyl system monomer, it is effective in a hot offset improvement. A cross-linking monomer is a monomer which has a carbon-carbon unsaturated double bond which can polymerize two or more. Specifically Aromatic divinyl compound; ethylene glycol dimethacrylate, such as divinylbenzene, divinylanthracene, and these derivatives, Diethylene nature unsaturated carboxylic acid ester, such as diethylene-glycol dimethacrylate; N,N-divinylaniline, A compound etc. which have three or more vinyl groups which have two vinyl groups, such as divinyl ether, such as a compound, pentaerythritol triaryl ether, and trimethylolpropane triacrylate, can be mentioned. In a polymer, a cross-linking polymer is two or more vinyl groups a polymer which it has, and specifically, Ester obtained by carrying out the condensation reaction of polymers which have two or more hydroxyl groups, such as polyethylene, polypropylene, polyester, and a polyethylene glycol, and the unsaturated carboxylic acid monomers, such as acrylic acid and methacrylic acid, to intramolecular can be mentioned. These cross-linking monomers and a cross-linking polymer are independent, respectively, or can be combined two or more sorts and can be used. Ten or less weight sections of the amount used are usually 0.1 – the amount part of duplexes preferably per monovinyl system monomer 100 weight section.

[0062]If a macro monomer is used with a monovinyl system monomer, since balance of preservability and low temperature fixability will become good, it is desirable. A macro monomer has a vinyl polymerization nature functional group at the end of a chain, and a number average molecular weight is usually oligomer or polymer of 1,000–30,000. If what has a small number average molecular weight is used, a surface portion of a polymer particle will become soft and preservability will come to fall. Conversely, if what has a large number average molecular weight is used, the melting nature of a macro monomer will worsen and fixability and preservability will come to fall. As a vinyl polymerization nature functional group in an end of a macro monomer chain, an acrylyl group, a methacryloyl group, etc. can be mentioned and a methacryloyl group is preferred from a viewpoint of the ease of carrying out of copolymerization.

[0063]As for a macro monomer, what has a glass transition temperature higher than glass transition temperature of a polymer produced by polymerizing said monovinyl system monomer is preferred. As an example of a macro monomer used for this invention, Although it is independent in styrene, a styrene derivative, methacrylic acid ester, acrylic ester, acrylonitrile, a methacrylonitrile, etc. or a polymer produced by polymerizing two or more sorts, a macro monomer which has a polysiloxane skeleton, etc. can be mentioned, A polymer produced by being independent or polymerizing combining these also in it in a thing especially methacrylic acid ester, or acrylic ester of hydrophilic nature is preferred. when using a macro monomer, the quantity receives monovinyl system monomer 100 weight section — usually — it is 0.05 to 1 weight section still more suitably 0.03 to 5 weight section suitably 0.01 to 10 weight section. If there is little quantity of a macro monomer, the preservability of a toner will not improve. If quantity of a macro monomer increases extremely, the fixability of a toner will come to fall.

[0064]Also in a polymerization nature monomer for cores, that in which glass transition temperature can usually form 60 ** or less of 40–60 ** polymers preferably is preferred as a monomer for cores. If glass transition temperature is too high, fixing temperature will become high, and if too conversely low, the preservability of a toner will fall. Usually, a monomer for cores may be used combining one sort or two sorts or more.

[0065]It is desirable that it is what gives a polymer which has a glass transition temperature higher than glass transition temperature of a polymer which constitutes a core particle as a polymerization nature monomer for shell. It is independent, respectively, or two or more sorts of monomers which form a polymer with glass transition temperature of greater than 80 **, such as styrene, acrylonitrile, and methyl methacrylate, as a monomer which constitutes a polymerization nature monomer for shell can be used, combining them. Glass transition temperature of a

polymer obtained by a polymerization nature monomer for shell is 50–130 ** usually 80–110 ** more preferably 60–120 ** in order to raise the preservation stability of polymerization toner. When lower than this, preservation stability may fall, and when conversely high, fixability may fall. Not less than 20 ** of differences of glass transition temperature between a polymer which consists of a polymerization nature monomer for cores, and a polymer which consists of a polymerization nature monomer for shell are not less than 10 ** usually not less than 30 ** more preferably. If smaller than this difference, preservability will fall.

[0066]As a polymerization initiator, persulfate; 4,4'-azobis, such as potassium persulfate (4-cyanovaleric acid), 2,2'-azobis (2-methyl-N-(2-hydroxyethyl) propionamide.) 2 and 2'-azobis (2-amidinopropane) dihydrochloride, Azo compounds, such as 2,2'-azobis (2,4-dimethylvaleronitrile) and 2,2'-azobisisobutyronitrile; Lauroyl peroxide, Benzoyl peroxide, t-butylperoxy 2-ethylhexanoate, t-hexyl peroxy 2-ethylhexanoate, t-butylperoxy perpivalate, Peroxides, such as di-isopropyl peroxy dicarbonate, 1, 1 and 3, and 3-tetramethyl butylperoxy 2-ethylhexanoate and t-butylperoxy isobuthylate, can be illustrated.

[0067]Also in these, it is preferred to choose an oil-soluble polymerization initiator as a polymerization nature monomer composition for cores, and it is preferred to choose a water-soluble polymerization initiator as a polymerization nature monomer composition for shell. A polymerization initiator for cores is **** for 0.5 – 10 weight sections still more preferably 0.3 to 15 weight section preferably 0.1 to 20 weight section to monovinyl system monomer 100 weight section. A polymerization initiator can also be added to suspension after an end of a granulation stage depending on the case, although it can add beforehand in a polymerization nature monomer composition. Quantity of a polymerization initiator for shell is a drainage system medium standard, and is usually 0.001 to 1 % of the weight. If this is small, a polymerization will not progress, but productivity falls, if conversely large, a molecular weight will fall and preservability will worsen.

[0068]In order to polymerize stably, dispersion stabilizer can be added to reaction mixture. As dispersion stabilizer, for example Sulfate; barium carbonate, such as barium sulfate and calcium sulfate, Phosphates, such as carbonate; calcium phosphate, such as calcium carbonate and magnesium carbonate; An aluminum oxide, Metallic compounds, such as metallic-oxides [, such as titanium oxide,], and aluminium hydroxide, Water soluble polymers, such as metal hydroxide; polyvinyl alcohol, such as magnesium hydroxide and a ferric hydroxide, methyl cellulose, and gelatin; an anionic surface-active agent, a nonionic surface-active agent, an ampholytic surface active agent, etc. can be mentioned, and these may be used independently or may use two or more kinds together. The dispersion stabilizer containing colloid of metallic compounds, especially metal hydroxide of difficulty water solubility can narrow particle size distribution of a polymer particle, and there is little ullage after washing of a dispersing agent, and since it can reproduce a picture vividly, it is [among these] preferred.

[0069]Dispersion stabilizer containing colloid of difficulty water solubility metal hydroxide, Colloid of metal hydroxide of difficulty water solubility obtained by adjusting the pH of solution of a water-soluble polyvalent metal compound to seven or more although there is no restriction by the process, It is preferred to use colloid of metal hydroxide of difficulty water solubility especially generated by the reaction in aqueous phase of a water-soluble polyvalent metal compound and hydroxylation alkali metal salt.

[0070]As for colloid of difficulty water soluble metallic compounds, in number particle size distribution, it is preferred that particle diameter Dp90 particle diameter Dp50 whose number total which measured from the diameter side of a granule is 50% is 0.5 micrometer or less, and is [90] 90% is 1 micrometer or less. If particle diameter of colloid becomes large, the stability of a polymerization will collapse and the preservability of a toner will fall.

[0071]A dispersion stabilizing agent is usually used at a rate of 0.1 to 20 weight section to monovinyl system monomer 100 weight section. If there are few these rates than 0.1 weight sections, it will be difficult to acquire sufficient polymerization stability, and will become easy to generate a polymerization aggregate. On the contrary, if 20 weight sections are exceeded, toner particle diameter after a polymerization becomes fine too much, and is not practical.

[0072]As a regulator, halogenated hydrocarbon [, such as mercaptans; carbon tetrachlorides,

such as t-dodecyl mercaptan, n-dodecyl mercaptan, and n-octyl mercaptan, and carbon tetrabromide,]; etc. can be mentioned, for example. These regulators can be added in the middle of a polymerization before a polymerization start. A regulator is usually preferably used at a rate of 0.1 to 5 weight section 0.01 to 10 weight section to monovinyl system monomer 100 weight section.

[0073]Although a toner of this invention remains as it is and is also applicable to development of electro photography, in order to adjust the electrostatic property of a toner, mobility, preservation stability, etc., it usually uses them for it, making particles (henceforth an external additive) of particle diameter smaller than this particle toner adhere or lay under the toner particle surface. An inorganic particle and organic resin particles are mentioned as an external additive. As an inorganic particle, a silica dioxide, an aluminum oxide, titanium oxide, a zinc oxide, tin oxide, barium titanate, strontium titanate, etc. are mentioned. As organic resin particles, methacrylate polymer particles, acrylic ester polymer particles, Core shell type particles etc. in which styrene methacrylic-acid-ester copolymer particles, styrene acrylic ester copolymer particles, zinc stearate, calcium stearate, and shell were formed in with a methacrylic-acid-ester copolymer, and a core was formed with a styrene polymer are mentioned. In the case of a magnetic one component system developer, oxides, such as iron, cobalt, nickel, an alloy that makes them a subject, or a ferrite, may also be included. An inorganic oxide particle, especially silica dioxide particles are [among these] preferred. Especially silica dioxide particles by which could carry out hydrophobing processing of these particle surfaces, and hydrophobing processing was carried out are preferred. Although quantity in particular of an external additive is not limited, it is usually 0.1 to 6 weight section to particle toner 100 weight section. An external additive may be used combining two or more sorts. When using combining an external additive, a method of combining the inorganic particles or an inorganic particle which differs in mean particle diameter, and organic resin particles is preferred. In order to make an external additive adhere to said particle toner, it teaches mixers, such as a Henschel mixer, and an external additive and particle toner are agitated and are usually performed. In adjusting a toner with an underwater polymerization mentioned above, after carrying out the agitation mix of the external additive to a water dispersing element of moisture handbill particle toner, a wet method, such as carrying out spray desiccation, can also be used.

[Translation done.]

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EXAMPLE

[Example]Next, although an example is given and this invention is explained in detail, this invention is not limited to these examples. The part in these examples and % are weight references as long as there is no special mention. It evaluated by this example by the following methods.

1. A polyester resin characteristic (1) number average molecular weight, the number average molecular weight of weight-average-molecular-weight polyester, and weight average molecular weight were computed as a standard polystyrene equivalent unit in accordance with the GPC method.

(2) The hydroxyl value of hydroxyl value polyester was measured according to the method indicated in 2, 4 and 9 of "standard fats-and-oils assay method" (Japanese oil recovery study association), and 2-83 paragraph. A unit is mgKOH/g.

(3) The glass transition temperature (T_g) of glass-transition-temperature polyester resin was measured according to the DSC method specified to JIS K 7121. A unit is **.

[0075]2. After taking out some of electrification control resin composition characteristic (1) colorant-dispersibility 1 positive or negative electrification control resin compositions, the toluene which dissolves electrification control resin was added and it was made the 5% solution of the electrification control resin composition. On the glass plate, the gap applied and dried the mixed solution with the doctor blade which is 30 micrometers, and produced the film. The major axis which observes this sheet with an optical microscope and exists in 100-micrometer square counted the number of a color particle of 0.2 micrometers or more.

[0076]3. The volume average particle diameter (dv) and number average particle diameters (dp) of the particle diameter toner of the toner characteristic (1) toner were measured by the multi-sizer (made by Beckman Coulter). Measurement by this multi-sizer was performed on diameter:of aperture100micrometer, the medium:iso ton II, and measurement-particles number:100000 piece conditions.

(2) The shape of the toner shape toner measured the value (rl/rs) which took the photograph with the scanning electron microscope, read the photograph with the nexus 9000 type image processing device, and broke the major axis of the toner by the minor axis. The measurement number of the toner at this time was performed by 100 pieces.

(3) Using the melt viscosity flow tester (the Shimadzu make, kind name "CFT-500C"), the amount of samples was set to 1.0-1.3g, it measured by the following measuring condition, and the melt viscosity at 120 ** was measured.

Starting temperature : 35 **, and part [for /] and heating-rate:3 ** preheating time: 5 minutes, cylinder pressure:10.0 Kgf/cm², Dice diameter : 0.5 mm, dice 1.0 mm in length, and 1g of shearing stress:2.451x10⁵Pa(4) THF insoluble daily dose toners are weighed precisely, It puts into a

thimble (the ADVANTEC Co., Ltd. make, 86R size of 28x100 mm), and it is applied to Soxhlet extractor, and THF is put into a lower flask and extracted for 6 hours. Extracting solvents were collected after extraction, and in the evaporator, after separation, the soluble pitch extracted in the extracting solvent was weighed precisely, and was computed from the following calculations. the amount (g) of THF insoluble daily dose (%) =(T-S) /T) x100T:toner samples

S: The amount (g) of extraction pitches

[0077](5) The volume specific resistance value of a volume specific resistance value toner, About 3 g of toners were put into a tablet molding machine 5 cm in diameter, the specimen was produced, having applied about 100 kg of load for 1 minute, and it was measured under with the temperature of 30 **, and a frequency of 1 kHz conditions using the dielectric loss measuring instrument (the Ando Electric Co., Ltd. make, kind name "TRS-10 type").

(6) The electrification quantity under electrification quantity L/L (temperature of 10 **, 20% of humidity), N/N (temperature of 23 **, 50% of humidity), and H/H (temperature [of 35 **], 80% of humidity) environment was measured, and the situation of the environmental variation was evaluated. The electrification quantity of a toner about a positive triboelectric charging toner. About the printer (the Brother Industries, Ltd. make, trade name "HL1670N") of commercial one ingredient of nonmagnetic development system, and a negative triboelectric charging toner. A toner is put into the printer (offing data company make, trade name "micro line 3010C") of commercial one ingredient of nonmagnetic development system, and five printed patterns of half-tone are printed after neglect under said environment one whole day and night. Then, the toner on a developing roller was attracted to the suction type electrification quantity measuring device, and the electrification quantity per unit weight was measured from electrification quantity and suction quantity.

(7) Optimum dose of toners were put on colorant dispersibility 2 slide glass, the cover glass was hung from on the, it was heated to 170 ** with the hot plate, and melting of the toner was carried out, next power was applied with the cover glass, and the toner was crushed. The major axis which observes the portion whose thickness of the toner measured by the thickness gage (the ANRITSU CORP. make, trade name:K-402B) is 20 micrometers with an optical microscope, and exists in 100-micrometer square counted the number of a color particle of 0.2 micrometers or more.

[0078]4. The print form was set to the printer which carried out the image evaluation (1) color tone above-mentioned, the toner was put into the developer, the neglect back was performed under the environment (H/H) of the temperature of 35 **, and 80% of humidity, solid printing was performed by concentration 5% one whole day and night, and it measured with the spectrum color difference meter (the Nippon Denshoku Co., Ltd. make, kind name "SE2000").

(2) Set a print form to the printer which carried out the printing density above-mentioned, and a toner is put into a developer, Perform the neglect back under the environment (H/H) of the temperature of 35 **, and 80% of humidity, and continuous printing is performed from the first stage by concentration 5% one whole day and night, Solid printing was performed at the time of the 20,000th sheet printing, black toner used McBETH transmission type image concentration measuring apparatus, color toner used the color reflection type densimeter (X-light company make, kind name "404A"), and printing density was measured.

One whole day and night using the printer which carried out the fogging above-mentioned under the environment (H/H) of the temperature of 35 **, and 80% of humidity (3) After neglect, Perform continuous printing by concentration 5%, and solid printing is performed after 20,000-sheet printing, Printing was stopped on the way, the toner of the nonimage area on the photo conductor after development was stripped off with adhesive tape (Sumitomo 3M make and Scotch whisky mending tape 810-3-18), and it was stuck on a new print form. Black toner measured the whiteness degree (B) of the print form which stuck the adhesive tape with the whiteness degree plan (made by Nippon Denshoku Co., Ltd.), and measured similarly the whiteness degree (A) of the print form which stuck only adhesive tape. Difference ΔY of the whiteness degree (A) and whiteness degree (B) was computed, and it was considered as the fogging value. On the other hand, like black toner, color toner measured the color tone instead of the whiteness degree, expressed as coordinates of Lab space using the above-mentioned spectrum color difference meter, respectively, computed color difference ΔE , and made it the fogging value. The one where this value is smaller shows that there is little fogging.

[0079](4) It converts so that the temperature of the fixing roll part of the printer which carried out the fixing temperature above-mentioned can be changed, the temperature of the fixing roll was changed, by 5 ** unit, the fixing rate of the developer in each temperature was measured,

and the fixing examination which asks for the relation between temperature and a fixing rate was done. Since a fixing rate stabilized the temperature of the changed fixing roll, it was neglected 5 minutes or more, and it was calculated from the ratio of the printing density before and behind tape peeling operation about the solid field of the paper which performed solid printing to the print form and was printed to it with the modified printer after that. That is, image concentration in front of ID and after tape exfoliation was carried out ID back, and the fixing rate computed the image concentration before tape exfoliation from the following formula.

fixing rate (%) = (after [ID] / before ID) × 100 — here, tape peeling operation sticks the adhesive tape mentioned above in the measured part of the examination paper, press it, it is made to adhere in a constant pressure, and is a series of operations of exfoliating adhesive tape in the direction which met paper with constant speed, after that. In this fixing examination, fixing roll temperature applicable to 80% of a fixing rate was made into the fixing temperature of a developer.

(5) Fixing roll temperature was changed as well as hot offset temperature fixing temperature measurement, solid printing was performed, and the temperature which hot offset generates was measured. Fixing roll temperature when hot offset occurred was made into hot offset temperature.

[0080][Composition of a hexahydro terephthalic acid screw (beta-hydroxyethyl)] 557 copies of 1,4-cyclohexanedicarboxylic acid and 443 copies of ethylene glycol were taught to the 3 Thu mouth flask provided with an agitator, the thermometer, the flowing-back condenser tube, the water sharing pipe, and the nitrogen gas introducing pipe. It stirs introducing nitrogen gas, and it was made to react at 180 ** for 5 hours, removing the water generated during a reaction. Reaction temperature was raised to 200 **, the pressure in a flask was reduced little by little, it was made 5 or less mmHg 1.5 hours afterward, the reaction was continued after that for further 2 hours, and the hexahydro terephthalic acid screw (beta-hydroxyethyl) was obtained. The hexahydro terephthalic acid screw (beta-hydroxyethyl) was a water-white fluid.

[0081][Composition of polyester resin]

(Synthetic example 1) In the 3 Thu mouth flask provided with an agitator, the thermometer, the flowing-back condenser tube, the water sharing pipe, and the nitrogen gas introducing pipe. 366 copies of 4-methyl-hexahydrophthalic anhydrides, 100 copies of hexahydro terephthalic acid screws (beta-hydroxyethyl), 100 copies of 5-amino hexahydro isophthalic acid dimethyl ester, 284 copies of 2,2-bis(4-hydroxy cyclohexyl)-propane, and 150 copies of ethylene glycol were taught. The total of a hydroxyl value [X]The total of /acid value The ratio of [Y] is 1.19. It stirs introducing nitrogen gas, and it was made to react at 200 ** for 3 hours, removing the alcohol generated during a reaction. Next, five copies of tetrabutoxy titanate was added, reaction temperature was raised to 220 **, the pressure in a flask was reduced little by little, it was made 5 or less mmHg 1.5 hours afterward, the reaction was continued after that for further 3 hours, and polyester resin (1) was obtained. 10,300 and a hydroxyl value were [the number average molecular weight / 68 mgKOH/g and the glass transition temperature of the obtained polyester resin (1) of 3,100 and weight average molecular weight] 62 **.

[0082](Synthetic example 2) In the 3 Thu mouth flask provided with an agitator, the thermometer, the flowing-back condenser tube, the water sharing pipe, and the nitrogen gas introducing pipe. 366 copies of 4-methyl-hexahydrophthalic anhydrides, 100 copies of hexahydro terephthalic acid screws (beta-hydroxyethyl), 150 copies of 5-sodium sulfoisophtharate dimethyl ester, 234 copies of 2,2-bis(4-hydroxy cyclohexyl)-propane, and 150 copies of ethylene glycol were taught. The total of a hydroxyl value [X]The total of /acid value The ratio of [Y] was 1.11. It stirs introducing nitrogen gas, and it was made to react at 200 ** for 3 hours, removing the alcohol generated during a reaction. Next, five copies of tetrabutoxy titanate was added, reaction temperature was raised to 220 **, the pressure in a flask was reduced little by little, it was made 5 or less mmHg 1.5 hours afterward, the reaction was continued after that for further 3 hours, and polyester resin (2) was obtained. 12,000 and a hydroxyl value were [the number average molecular weight / 52 mgKOH/g and the glass transition temperature of the obtained polyester resin (2) of 3,400 and weight average molecular weight] 63 **.

[0083](Synthetic example 3) 317 copies of hexahydrophthalic acid, 329 copies of terephthalic

acid, 304 copies of neopentyl glycol, and 50 copies of trimethylolpropane were taught to the 3 Thu mouth flask provided with an agitator, the thermometer, the flowing-back condenser tube, the water sharing pipe, and the nitrogen gas introducing pipe. The total of a hydroxyl value [X] The total of /acid value The ratio of [Y] is 1.10. It stirs introducing nitrogen gas, and it was made to react at 200 ** for 3 hours, removing the alcohol generated during a reaction. Next, 0.5 copy of zinc acetate was added, reaction temperature was raised to 220 **, the pressure in a flask was reduced little by little, it was made 5 or less mmHg 1.5 hours afterward, the reaction was continued after that for further 3 hours, and polyester resin (3) was obtained. 5,500 and a hydroxyl value were [the number average molecular weight / 72 mgKOH/g and the glass transition temperature of the obtained polyester resin (3) of 2,900 and weight average molecular weight] 53 **.

[0084][Manufacture of a positive electrification control resin composition] (reference example 1) 100 copies of polyester resin (1) obtained in the synthetic example 1 was made to distribute 24 copies of methyl ethyl ketone, and six copies of methanol as electrification control resin, and it kneaded with a roll, cooling. In the place where electrification control resin coiled around the roll, magenta pigment (client company make, trade name "C. I. pigment violet 19") 100 weight section was added gradually, kneading was performed for 1 hour, and the electrification control resin composition (1-1) was manufactured. At this time, a mill opening is 1 mm the first stage. The gap was extended gradually after that, the last was extended to 3 mm, and the organic solvent (methyl-ethyl-ketone/methanol =4/1 partially aromatic solvent) was set by the kneading state of electrification control resin, and was added several times.

After taking out some electrification control resin compositions, add toluene, and it was made to dissolve and was made the 5% solution of the electrification control resin composition of toluene. On the glass plate, the gap applied and dried the mixed solution with the doctor blade which is 30 micrometers, and produced the sheet. When this sheet was observed with the optical microscope, as for a color particle of 0.2 micrometers or more, the major axis which exists in 100-micrometer square did not exist.

[0085](Reference examples 2-3) As colorant, instead of a magenta pigment (client company make, trade name "C. I. pigment violet 19"), Cyanogen paints (client company make, trade name "C. I. pigment blue 15:3") or a yellow pigment (client company make, trade name "C. I. pigment yellow 180") was used, and also the right electrification control resin composition (1-2 and 1-3) was obtained like the reference example 1. The result of the colorant dispersibility 1 at this time is shown in Table 1.

[0086][Manufacture of a negative electrification control resin composition] (reference examples 4-6) The negative electrification control resin composition (2-1 to 2-3) was obtained like the reference examples 1-3 except having used the polyester resin (2) obtained in the synthetic example 2 instead of polyester resin (1). The result of the colorant dispersibility 1 at this time is shown in Table 1.

[0087][Manufacture of a resin composition] The resin composition (3-1 to 3-3) was obtained like the reference examples 1-3 except having used the polyester resin (3) obtained in the synthetic example 3 instead of polyester resin (1). The result of the colorant dispersibility 1 at this time is shown in Table 1.

[0088]

[Table 1]

【表 1】

	参考例								
	1	2	3	4	5	6	7	8	9
顔料の種類	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー
量 (部)	100	100	100	100	100	100	100	100	100
ポリエステル樹脂 (1)	100	100	100		100	100			
ポリエステル樹脂 (2)				100					
ポリエステル樹脂 (3)									
樹脂組成物	1-1	1-2	1-3	2-1	2-2	2-3	3-1	3-2	3-3
着色剤分散性 1 (個)	0	0	0	0	0	1	74	63	94

[0089][Manufacture of a toner]

(Example 1) In the solution which dissolved 9.8 copies of magnesium chlorides (water-soluble polyvalent metallic salt) in 250 copies of ion exchange water. It added gradually under stirring of the solution which dissolved 6.9 copies of sodium hydroxide (hydroxylation alkaline metal) in 50 copies of ion exchange water, and magnesium hydroxide colloid (metal hydroxide colloid of difficulty water solubility) dispersion liquid were prepared. Number-average-particle-diameters D50 (50% accumulated of number particle size distribution) and D90 of the drop (90% accumulated of number particle size distribution) measured the particle size distribution of said generated colloid with the size distribution measuring device (the Shimadzu Corp. make, kind name "SALD2000A type"). In measurement by this particle-size-distribution measuring instrument, it carried out on condition of salt solution use 10% as carrier fluid at the time of drop measurement for [refractive-index =1.55-0.20i and ultrasonic-exposure-time =] 5 minutes. 80.5 copies of styrene, 19.5 copies of butyl acrylates, 0.5 copy of divinylbenzene, and a polymethacrylic-acid-ester macro monomer (the Toagosei chemical industry company make.) A trade name "AA6", Tg = The polymerization nature monomer for cores which consists of 0.3 copy of 94 **, Wet milling was performed for 11 copies of right electrification control resin

compositions (1-1) mentioned above, one copy of negative electrification control resin composition (2-1), two copies of t-dodecyl mercaptans, and dipentaerythritol hexa Millis Tait 10 copy using the media type wet grinding mill, and the polymerization nature monomer composition for cores was obtained. On the other hand, two copies of methyl methacrylate and 100 copies of water were micro-disperse-ization-processed with the ultrasonic emulsification machine, and the water dispersion of the polymerization nature monomer for shell was obtained. Dp90 was 1.6 micrometers when the particle diameter of the drop of the polymerization nature monomer for shell was measured with said size distribution measuring device.

[0090] Said monomer composition for cores is fed into the magnesium hydroxide colloidal dispersion liquid obtained with the above, stirring until a drop is stabilized — there — t-butylperoxy2-ethylhexanoate (the Nippon Oil & Fats Co., Ltd. make.) Trade name "par butyl O" After adding five copies, using EBARAMAIRUDA (the Ebara Corp. make, kind name "MDN303V"), quantity shearing stirring during 30 minutes was carried out at the number of rotations of 15,000 rpm, and the drop of the monomer composition was corned. When put the water dispersion of this corned polymerization nature monomer composition for cores into the reactor equipped with stirring wings, a polymerization reaction was made to start at 90 ** and polymerization conversion reached to about 100%, it sampled and the particle diameter of the core was measured. As a result, volume average particle diameter (dv) was 7.3 micrometers. The water dispersion and 2,2'-azobis (2-methyl- N. -(2-hydroxyethyl)- the solution which dissolved 0.2 copy of propionamide (the Wako Pure Chem make, trade name "VA-086") in 65 copies of distilled water was put into the reactor) of said polymerization nature monomer for shell After continuing a polymerization for 8 hours, the reaction was suspended and the water dispersion of pH 9.5 particle toner was obtained.

[0091] After making pH of the system or less into five with sulfuric acid, performing acid cleaning (for 25 ** and 10 minutes) and filtration separating water, stirring the water dispersion of the particle toner obtained with the above, 500 copies of ion exchange water was newly added and re-slurred, and backwashing by water was performed. Then, again, after the repetition line carried out filtering separation of the solid content for drying and backwashing by water several times, the dryer performed 2 day-and-night desiccation at 45 **, and particle toner was obtained. The volume average particle diameter (dv) which took out and measured dry particle toner was 7.3 micrometers, and volume-average-particle-diameter (dv) / number average particle diameters (dp) were 1.21. rl/rs was 1.1 and the amount of gels was 15%. The number of color particles of 0.2 micrometers or more did not have a major axis which exists in an unit area. To 100 copies of particle toner obtained with the above, 0.6 copy of colloidal silica (the Clariant, LTD. make, trade name "HDK2150") by which hydrophobing processing was carried out was added, it mixed to it using the Henschel mixer, and the positive triboelectric charging toner was prepared. The obtained evaluation of the characteristic of a toner, a picture, etc. is shown in Table 2.

[0092] (Examples 2-3) In Example 1, the quantity of the right electrification control resin composition to be used and a negative electrification control resin composition was changed as shown in Table 2, and also the positive triboelectric charging toner was obtained like Example 1. The characteristic of a toner and the evaluation result of a picture which were obtained are shown in Table 2.

[0093] (Comparative examples 1-3) In Example 1, instead of using a right electrification control resin composition and a negative electrification control resin composition, The polymerization nature monomer composition for cores was produced by the formula of Table 2 using the quarternary-ammonium-salt charge controlling agent (Orient chemical industry company make, trade name "BONTORON P-51") as the resin composition (3-1) obtained by the reference example 7, and a charge controlling agent, and also the positive triboelectric charging toner was obtained like Example 1. The obtained evaluation of the characteristic of a toner, a picture, etc. is shown in Table 2. Here, the amount of right charge controlling agents was controlled, and the positive triboelectric charging toner of the comparative examples 1-3 was manufactured so that the electrification quantity which the kind of colorant measures at the same positive triboelectric charging toner of Examples 1-3, and the temperature of 23 ** and 50% of humidity might become

the same.

[0094]

[Table 2]

[表 2]

	実施例			比較例		
	1	2	3	1	2	3
顔料の種類	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー
正帯電樹脂組成物 (1-1)	11					
(1-2)		10.5				
(1-3)			10			
負帯電樹脂組成物 (2-1)	1					
(2-2)		1.5				
(2-3)			2			
樹脂組成物 (3-1)				12		
(3-2)					12	
(3-3)						12
正帯電制御剤				1	1.5	2
トナー特性						
d _v (μm)	7.3	7.1	7.2	7.4	7.2	7.5
d _v /d _p	1.21	1.22	1.21	1.25	1.25	1.28
形状 (r ₁ /r _s)	1.1	1.2	1.1	1.2	1.2	1.3
熔融粘度 (Pa·s)	7400	8100	6900	8500	8600	7900
THF不溶分量 (%)	15	20	18	35	27	36
体積固有抵抗 (log (Ω·cm))	11.4	11.7	11.5	11.6	11.3	11.5
官能基量比 (P:Q)	1:0.09	1:0.15	1:0.21	—	—	—
L/L帯電 (μC/g)	24	26	26	45	38	56
N/N帯電 (μC/g)	24	25	24	24	25	24
H/H帯電 (μC/g)	23	23	22	10	7	22
着色剤分散性 2 (個)	0	1	1	85	71	65
画質評価						
色調 L *	62.2	69.3	95.8	71.6	76.7	95.9
a *	76.9	-19.3	-18.2	51.5	-18.2	-16.8
b *	-28.3	-40.4	83.9	-21.2	-29.3	65.8
印字濃度	1.45	1.48	1.47	1.35	1.38	1.39
カブリ	0.3	0.3	0.7	8.7	14.1	3.6
定着温度 (°C)	130	130	125	145	140	145
オフセット発生温度 (°C)	220	220	220	220	220	220

[0095](Examples 4-6) In Example 1, the quantity of the right electrification control resin composition to be used and a negative electrification control resin composition was changed as shown in Table 2, and also the negative triboelectric charging toner was obtained like Example 1. The characteristic of a toner and the evaluation result of a picture which were obtained are shown in Table 3.

[0096](Comparative examples 4-6) In Example 1, instead of using a right electrification control resin composition and a negative electrification control resin composition, The polymerization nature monomer composition for cores was produced by the formula of Table 3 using the salicylic acid metal salt charge controlling agent (Orient chemical industry company make, trade name "BONTORON E-84") as the resin composition (3-1) obtained by the reference example 7, and a charge controlling agent, and also the negative triboelectric charging toner was obtained like Example 1. The obtained evaluation of the characteristic of a toner, a picture, etc. is shown in Table 3. Here, the amount of negative electrification controlling agents was controlled, and the negative triboelectric charging toner of the comparative examples 4-6 was manufactured so that the electrification quantity which the kind of colorant measures at the same negative triboelectric charging toner of Examples 4-6, and the temperature of 23 ** and 50% of humidity might become the same.

[0097]

[Table 3]

【表 3】

	実施例			比較例		
	4	5	6	4	5	6
顔料の種類	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー
正帯電樹脂組成物 (1-1)	2					
(1-2)		1.5				
(1-3)			1			
負帯電樹脂組成物 (2-1)	10					
(2-2)		10.5				
(2-3)			11			
樹脂組成物 (3-1)				12		
(3-2)					12	
(3-3)						12
負帯電制御剤				2	1.5	0.8
トナー特性						
d _v (μm)	7.1	7.0	7.1	7.2	7.1	7.3
d _v /d _p	1.22	1.21	1.21	1.27	1.24	1.30
形状 (r ₁ /r _s)	1.1	1.2	1.1	1.2	1.2	1.3
熔融粘度 (Pa·s)	7500	7400	6800	9200	8400	7700
THF不溶分量 (%)	21	19	23	38	28	31
体積固有抵抗 (log (Ω·cm))	11.5	11.6	11.7	11.7	11.3	11.6
官能基量比 (P:Q)	0.21:1	0.13:1	0.09:1	—	—	—
L/L帯電 (μC/g)	-23	-23	-24	-40	-28	-66
N/N帯電 (μC/g)	-22	-22	-23	-22	-22	-23
H/H帯電 (μC/g)	-21	-20	-21	-18	-19	-20
着色剤分散性 2 (個)	2	0	1	96	69	78
画質評価						
色調 L*	56.9	75.5	87.3	67.2	81.4	87.8
a*	78.1	-30.2	-17.9	47.4	-22.5	-13.3
b*	-34.4	-30.4	77.6	-23.3	-20.3	48.2
印字濃度	1.55	1.54	1.49	1.37	1.37	1.38
カブリ	0.1	0.3	0.5	4.2	5.6	3.3
定着温度 (°C)	130	135	130	145	145	140
オフセット発生温度 (°C)	220	220	220	220	220	220

[0098] From Tables 2 and 3. The polycondensation of the polyhydric alcohol (A2) containing the polyvalent-carboxylic-acid compound (A1) which contains an amino group or its salt as right electrification control resin and/or an amino group, or its salt is carried out. The toner of the comparative examples 1-6 which carry out the polycondensation of the polyhydric alcohol (J2) containing the polyvalent-carboxylic-acid compound (J1) which contains a sulfonic group or its salt as the becoming polyester resin and negative electrification control resin and/or a sulfonic group, or its salt and which do not carry out polyester resin content, Electrification quantity is understood that pigment dispersibility and a color tone are bad, printing density's are low, and there are in fogging. [many] On the other hand, the toner of this invention has high environmental stability, pigment dispersibility and a color tone are good, printing density is high, and it turns out that fogging can also be lessened.

[Translation done.]

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(54) 【発明の名称】 トナー及びその製造方法

(57) 【要約】

【課題】 電子写真に於いて、鮮明な画像を得ることができ、異なる環境下に置かれても帯電性が変化しないトナー及びその製造方法を提供すること。特にカラートナーに適用した場合、カラー画像の鮮明な色調の再現に必要な透明性等の分光特性に優れ、カブリが少なく、印字濃度を高くすることができ、更に耐久印字性にも優れたトナー及びその製造方法を提供すること。

【解決手段】 結着樹脂、着色剤、正帯電制御樹脂及び負帯電制御樹脂を含有し、該正帯電制御樹脂がアミノ基若しくはその塩を含有する多価カルボン酸化合物(A1)及び／又はアミノ基若しくはその塩を含有する多価アルコール(A2)を重縮合してなるポリエステル樹脂であり、該負帯電制御樹脂がスルホン酸基若しくはその塩を含有する多価カルボン酸化合物(J1)及び／又はスルホン酸基若しくはその塩を含有する多価アルコール(J2)を重縮合してなるポリエステル樹脂であるトナー。

【特許請求の範囲】

【請求項1】 結着樹脂、着色剤、正帯電制御樹脂及び負帯電制御樹脂を含有し、該正帯電制御樹脂がアミノ基若しくはその塩を含有する多価カルボン酸化合物（A1）及び／又はアミノ基若しくはその塩を含有する多価アルコール（A2）を重縮合してなるポリエステル樹脂であり、該負帯電制御樹脂がスルホン酸基若しくはその塩を含有する多価カルボン酸化合物（J1）及び／又はスルホン酸基若しくはその塩を含有する多価アルコール（J2）を重縮合してなるポリエステル樹脂であるトナ

ー。
【請求項2】 加熱溶融して膜厚20 μ mにしたトナーの面積100 μ m \times 100 μ m中に観察される長径0.2 μ m以上の着色剤粒子数が50個以下である請求項1記載のトナー。

【請求項3】 アミノ基若しくはその塩を含有する多価カルボン酸化合物（A1）及び／又はアミノ基若しくはその塩を含有する多価アルコール（A2）を重縮合してなるポリエステル樹脂からなる正帯電制御樹脂100重量部と、着色剤10～200重量部と、該正帯電制御樹脂を溶解し得る有機溶剤0～100重量部とを混合して、正帯電制御樹脂組成物を得る工程、並びにスルホン酸基若しくはその塩を含有する多価カルボン酸化合物（J1）及び／又はスルホン酸基若しくはその塩を含有する多価アルコール（J2）を重縮合してなるポリエステル樹脂からなる負帯電制御樹脂100重量部と、着色剤10～200重量部と、該負帯電制御樹脂を溶解し得る有機溶剤0～100重量部とを混合して、負帯電制御樹脂組成物を得る工程とを有することを特徴とするトナーの製造方法。

【請求項4】 前記正帯電制御樹脂組成物0.1～20重量部と、前記負帯電制御樹脂組成物0.1～20重量部と、重合性単量体100重量部とを混合して重合性単量体組成物を得、この組成物を水系分散媒体中で重合することを含む請求項3記載のトナーの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、トナー及びその製造方法に関するものである。詳細には、一成分方式、二成分方式にかかわらず、鮮明な色調と、安定した帯電と、優れた転写性を有するトナー及びその製造方法に関する。

【0002】

【従来の技術】近年、フルカラー電子写真装置、特にデジタル化されたフルカラー電子写真装置が注目されてきており、OA化の伸展に伴って広く市場に展開されつつある。電子写真装置に用いられる電子写真用トナー（以下、単に「トナー」ということがある。）としては、主に、結着樹脂に、着色剤、帯電制御剤等を加えて混練し、次いで粉碎、さらに分級する、いわゆる粉碎法によ

って製造される粒子（粉碎法粒子）、又は、重合性単量体、着色剤、帯電制御剤等の混合物を懸濁重合、乳化重合、分散重合などの方法で重合して、必要に応じて会合させることによって製造される粒子（重合法粒子）が主に用いられている。また、感光体の帯電方式によって、それに用いられるトナーが異なり、負帯電性のトナーと正帯電性のトナーに分類されている。

【0003】電子写真法においても最近ではカラー化が進み、カラー画像形成装置に対応するカラートナーが求められている。カラー画像形成装置には、複数の画像形成部を備え、各画像形成部でそれぞれ色の異なるトナー像を形成し、イエロー、マゼンタ、シアン、ブラックなどのカラートナー像を同一の記録媒体に順次重ね転写してカラー印刷を行うことが知られている。粉碎トナーや重合トナー等のいずれを使用するにしても、カラートナーとして使用されるには以下のようなことが要求されている。

【0004】（1）多色重ねをするためにトナーは透明性が高いこと。

（2）色を再現させるために分光反射特性が優れること。

（3）トナーの正または負の帯電を精密に制御すること。

（4）低温定着が可能であること。

（5）カラートナーの製造が容易であること。

【0005】これらの要求に応えるために種々の検討が行われている。例えば特開昭61-149969号公報には、アミン含有単量体の均質重合体等の帯電強化用添加剤と、顔料とを、クロロホルム等のハロゲン化炭化水素中、ロールミルで混合して調製した帯電強化用添加剤で処理された顔料を、樹脂粒子と溶融混合後、粉碎するトナー組成物が開示されている。特開昭62-119549号公報には、結着樹脂を溶剤に溶解し、この溶液中に着色剤、帯電制御剤を加え、攪拌混合後、凍結乾燥法により溶剤を除去し、次いで得られたトナーを粉碎分級するトナー製造方法が開示されている。特開平03-155568号公報には、結着樹脂と、染料及び顔料の少なくとも1つと、有機溶剤とを混合混練し、染料あるいは顔料のマスターバッチを製造し、このマスターバッチをさらに結着樹脂、及び必要に応じてその他の添加剤とを混合、混練、粉碎分級するトナーの製造方法が開示されている。また、特開平4-242752号公報には、結着樹脂中で顔料を加熱、加圧混練して得られた樹脂分散型顔料を、結着樹脂と溶融・混練し、分散するカラートナーの製造方法、及び結着樹脂中に存在する円形相当径で0.3 μ m以上の顔料粒子の個数割合が0.1%以下で分散しているカラートナーが開示されている。

【0006】しかしながらこれらの方法によっても、前記カラートナーの種々の要求を同時に満足することは相当地に困難である。特に、安定した帯電性を有し、透明性

に優れ、かつ分光反射特性の良好なカラートナーを製造することは困難であった。

【0007】

【発明が解決しようとする課題】本発明の目的は、電子写真に於いて、鮮明な画像を得ることができ、異なる環境下に置かれても帯電性が変化しないトナー及びその製造方法を提供することにある。特にカラートナーに適用した場合、カラー画像の鮮明な色調の再現に必要な透明性等の分光特性に優れ、カブリが少なく、印字濃度を高くすることができ、更に耐久印字性にも優れたトナー及びその製造方法を提供することにある。本発明者は、上記目的を達成するために鋭意研究を重ねた結果、特定のポリエステル樹脂からなる正帯電制御樹脂と負帯電制御樹脂とを用いることで、前記目的を達成できることを見だし、本発明を完成するに至った。

【0008】

【課題を解決するための手段】かくして、本発明によれば、(1) 結着樹脂、着色剤、正帯電制御樹脂及び負帯電制御樹脂を含有し、該正帯電制御樹脂がアミノ基若しくはその塩を含有する多価カルボン酸化合物(A1)及び/又はアミノ基若しくはその塩を含有する多価アルコール(A2)を重縮合してなるポリエステル樹脂であり、該負帯電制御樹脂がスルホン酸基若しくはその塩を含有する多価カルボン酸化合物(J1)及び/又はスルホン酸基若しくはその塩を含有する多価アルコール(J2)を重縮合してなるポリエステル樹脂であるトナー、(2) アミノ基若しくはその塩を含有する多価カルボン酸化合物(A1)及び/又はアミノ基若しくはその塩を含有する多価アルコール(A2)を重縮合してなるポリエステル樹脂からなる正帯電制御樹脂100重量部と、着色剤10~200重量部と、該正帯電制御樹脂を溶解し得る有機溶剤0~100重量部とを混合して、正帯電制御樹脂組成物を得る工程、並びにスルホン酸基若しくはその塩を含有する多価カルボン酸化合物(J1)及び/又はスルホン酸基若しくはその塩を含有する多価アルコール(J2)を重縮合してなるポリエステル樹脂からなる負帯電制御樹脂100重量部と、着色剤10~200重量部と、該負帯電制御樹脂を溶解し得る有機溶剤0~100重量部とを混合して、負帯電制御樹脂組成物を得る工程とを有することを特徴とするトナーの製造方法、が提供される。

【0009】

【発明の実施の形態】本発明のトナーは、少なくとも結着樹脂、着色剤、正帯電制御樹脂及び負帯電制御樹脂を含有する。本発明のトナーに含有される正帯電制御樹脂は、アミノ基若しくはその塩を含有する多価カルボン酸化合物(A1)及び/又はアミノ基若しくはその塩を含有する多価アルコール(A2)を重縮合してなるポリエステル樹脂からなるものである。尚、後述するアミノ基若しくはその塩を含有する多価カルボン酸化合物(A

1) 及び/又はアミノ基若しくはその塩を含有する多価アルコール(A2)と共重縮合できるその他の多価カルボン酸化合物や多価アルコールには、アミノ基若しくはその塩を含有しない。

【0010】正帯電制御樹脂としてのポリエステル樹脂を構成するアミノ基若しくはその塩を含有する多価カルボン酸化合物(A1)としては、アミノテレフタル酸、5-アミノイソフタル酸、5-アミノイソフタル酸メチルエステル、4-アミノフタル酸、4-アミノフタル酸無水物、4-アミノナフタレン-2, 7-ジカルボン酸、5-[4-アミノフェノキシ]イソフタル酸などの芳香族多価カルボン酸；5-アミノヘキサヒドロイソフタル酸、5-アミノヘキサヒドロイソフタル酸メチルエステル、4-アミノヘキサヒドロフタル酸、4-アミノヘキサヒドロフタル酸無水物；5-アミノテトラヒドロイソフタル酸、5-アミノテトラヒドロイソフタル酸メチルエステル、4-アミノテトラヒドロフタル酸、4-アミノテトラヒドロフタル酸無水物等の脂環族多価カルボン酸；等が挙げられる。また、アミノ基若しくはその塩を含有する多価アルコール(A2)としては、2-アミノ-2-メチル-1, 3-プロパンジオール、ジエタノールアミン等の鎖状脂肪族多価アルコール；2-アミノ-4-ヒドロキシメチルベンジルアルコール、2-アミノ-3-ヒドロキシメチルベンジルアルコール、4-アミノ-2-ヒドロキシメチルベンジルアルコール、5-アミノ-3-ヒドロキシメチルベンジルアルコール等の芳香族多価アルコール；2, 4-ビス(ヒドロキシエチル)-1-アミノシクロヘキサンなど脂環族多価アルコール；及びそれらのアンモニウム塩が挙げられる。

【0011】アンモニウム塩を有するポリエステル樹脂は、上記のごときアンモニウム塩を有する多価カルボン酸化合物(A1)及び/又はアンモニウム塩を有する多価アルコール(A2)が共重縮合されたものであってもよいし、アミノ基を有する多価カルボン酸化合物(A1)及び/又はアミノ基を有する多価アルコール(A2)を共重縮合させた後でアンモニウム塩化したものでもよい。本発明のトナーに含有される正帯電制御樹脂としてのポリエステル樹脂において、アミノ基若しくはその塩を含有する多価カルボン酸化合物(A1)及び/又はアミノ基若しくはその塩を含有する多価アルコール(A2)の量は、ポリエステル樹脂を構成する全単量体(全カルボン酸成分と全アルコール成分との合計)の、通常、0.2~30モル%、好ましくは、0.5~10モル%である。この多価カルボン酸化合物(A1)及び/又は多価アルコール(A2)を重縮合成分として含有することによって、トナー中の顔料の分散性が向上し、トナーの帯電性を制御することができる。

【0012】正帯電制御樹脂としてのポリエステル樹脂は、さらに環式2価カルボン酸化合物(B)が共重縮合されていることが好ましい。環式2価カルボン酸化合物

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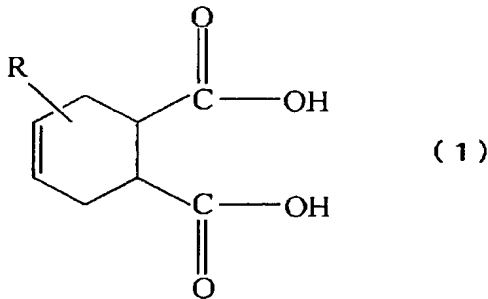
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(B)としては、芳香族2価カルボン酸化合物及び脂環族2価カルボン酸化合物が挙げられ、脂環族2価カルボン酸化合物が好ましい。芳香族2価カルボン酸化合物としては、1,5-ナフタル酸、2,6-ナフタル酸、ジフェン酸、テレフタル酸、イソフタル酸、フタル酸及びこれらのアルキル置換体、並びにこれらの酸無水物、ハロゲン化物、エステル、アミドなどの誘導体が挙げられる。

【0013】脂環族2価カルボン酸化合物は、脂環構造と2個のカルボキシル基又はカルボン酸誘導体基とが分子構造中に存在する化合物である。脂環構造としては、シクロペンタン環、シクロヘキサン環、シクロヘプタン環、シクロヘキセン環などの単環；ノルボルナン環、ノルボルネン環などの多環のものが挙げられる。好適な脂環族2価カルボン酸化合物としては、カルボキシル基又はカルボン酸誘導体基（アミド基、エステル基、酸無水物基、酸ハロゲン化物）が、脂環を構成する2個の炭素原子それぞれに結合してなる脂環族2価カルボン酸化合物；特に一般式（1）又は（2）で表される脂環族2価カルボン酸またはそれらの無水物のようなアルキル基が脂環に置換基として結合しているものである。なお、アルキル基としては、好ましくは炭素数1～8個のもの、具体的にはメチル基、エチル基、プロピル基、イソプロピル基などが挙げられる。

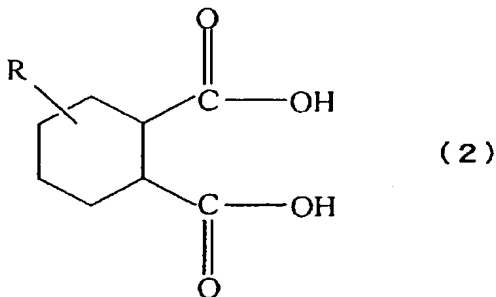
【0014】

【化1】



【0015】

【化2】



【0016】式（1）又は（2）中のRは、アルキル基である。

【0017】正帯電制御樹脂としてのポリエステル樹脂に好ましく用いられる脂環族2価カルボン酸化合物は、たとえば、ブタジエン、イソブレン、ビベリレン、シクロペンタジエンなどのジエン化合物と；無水マレイン酸とを反応させ、必要に応じて水素化すること等によって得られる。脂環族2価カルボン酸化合物の具体例としては、テトラヒドロテレフタル酸、テトラヒドロイソフタル酸、テトラヒドロフタル酸；ヘキサヒドロテレフタル酸、ヘキサヒドロイソフタル酸、ヘキサヒドロフタル酸；3-アルキルテトラヒドロテレフタル酸、4-アルキルテトラヒドロテレフタル酸、3-アルキルテトラヒドロイソフタル酸、4-アルキルテトラヒドロイソフタル酸、3-アルキルテトラヒドロフタル酸、4-アルキルテトラヒドロフタル酸；3-アルキルヘキサヒドロテレフタル酸、4-アルキルヘキサヒドロテレフタル酸、3-アルキルヘキサヒドロイソフタル酸、4-アルキルヘキサヒドロイソフタル酸、3-アルキルヘキサヒドロフタル酸、4-アルキルヘキサヒドロフタル酸；3,6-エンドメチレン-テトラヒドロテレフタル酸、3,6-エンドメチレン-テトラヒドロイソフタル酸、3,6-エンドメチレン-テトラヒドロフタル酸；3,6-エンドメチレン-ヘキサヒドロテレフタル酸、3,6-エンドメチレン-ヘキサヒドロイソフタル酸、3,6-エンドメチレン-ヘキサヒドロフタル酸；

【0018】2-アルキル-3,6-エンドメチレン-テトラヒドロテレフタル酸、3-アルキル-3,6-エンドメチレン-テトラヒドロテレフタル酸、2-アルキル-3,6-エンドメチレン-テトラヒドロイソフタル酸、3-アルキル-3,6-エンドメチレン-テトラヒドロイソフタル酸、2-アルキル-3,6-エンドメチレン-テトラヒドロフタル酸、3-アルキル-3,6-エンドメチレン-テトラヒドロフタル酸；2-アルキル-3,6-エンドメチレン-ヘキサヒドロテレフタル酸、3-アルキル-3,6-エンドメチレン-ヘキサヒドロテレフタル酸、2-アルキル-3,6-エンドメチレン-ヘキサヒドロイソフタル酸、3-アルキル-3,6-エンドメチレン-ヘキサヒドロイソフタル酸、2-アルキル-3,6-エンドメチレン-ヘキサヒドロフタル酸、3-アルキル-3,6-エンドメチレン-ヘキサヒドロフタル酸；が挙げられる。

【0019】脂環族2価カルボン酸化合物の誘導体の具体例としては、テトラヒドロフタル酸無水物、ヘキサヒドロフタル酸無水物、3-アルキルテトラヒドロフタル酸無水物、3-アルキルヘキサヒドロフタル酸無水物、4-アルキルテトラヒドロフタル酸無水物、4-アルキルヘキサヒドロフタル酸無水物などの酸無水物；ハロゲン化物、エステル、アミド等が挙げられる。これらは、それぞれ単独で、あるいは2種以上を組み合わせる用いることができる。これらの中でも、3-アルキルテトラヒドロフタル酸、3-アルキルヘキサヒドロフタル酸、

4-アルキルテトラヒドロフタル酸、4-アルキルヘキサヒドロフタル酸およびこれらの無水物が、溶融特性が高くなり、トナーに該ポリエステル樹脂を用いた場合には着色剤の分散性に優れたトナーが得られるので好ましい。環式2価カルボン酸化合物(B)の量は、ポリエステル樹脂を構成する全多価カルボン酸成分の、通常、70~100モル%、特に、80~100モル%であることが好ましい。この割合が少ないと、トナーの十分な保存性が得られないことがある。

【0020】正帯電制御樹脂としてのポリエステル樹脂を構成するカルボン酸成分として、必要に応じて、鎖式2価カルボン酸化合物(D)や3価以上のカルボン酸化合物(F)が共重縮合されていてもよい。共重縮合可能な鎖式2価カルボン酸化合物(D)としては、コハク酸、アジピン酸、アゼライン酸、セバシン酸、ドデカンジカルボン酸、フマル酸、マレイン酸、イタコン酸などが挙げられる。3価以上の多価カルボン酸化合物(F)としては、トリメリット酸、ピロメリット酸、トリメジン酸などが挙げられる。鎖式2価カルボン酸化合物

(D)の割合は、全カルボン酸成分の30モル%以下が好ましい。この割合が大きくなると、ガラス転移温度や溶融粘度が低くなり、トナーの耐ブロッキング性が低下したり、ホットオフセットが発生したりすることがある。3価以上の多価カルボン酸化合物(F)の割合は、全カルボン酸成分の5モル%以下が好ましい。この割合が大きくなると、ポリエステル樹脂の重量平均分子量が高くなるために、トナーの溶融粘度が高くなり、トナーの定着性が悪くなることがある。

【0021】本発明のトナーに含有される正帯電制御樹脂としてのポリエステル樹脂は、さらに環式2価アルコール(C)が共重縮合されていることが好ましい。環式2価アルコール(C)としては、芳香族2価アルコールと脂環族2価アルコールが挙げられ、脂環族2価アルコールが好ましい。芳香族2価アルコールとしては、パラキシリレンジグリコール、メタキシリレンジグリコール、オルトキシリレンジグリコール、1,4-フェニレンジグリコールのエチレンオキシド付加物、ビスフェノールAのエチレンオキシド付加物およびプロピレンオキシド付加物などが挙げられる。脂環族2価アルコールとしては、2,2-ビス(4-ヒドロキシシクロヘキシル)プロパン(すなわち、水素化ビスフェノールA)、1,4-ビス(ヒドロキシメチル)シクロヘキサン、1,3-ビス(ヒドロキシメチル)シクロヘキサン、1,2-ビス(ヒドロキシメチル)シクロヘキサン、2,2,4,4-テトラメチル-1,3-シクロヘキサジオール、1,4-シクロヘキサジオール、水素化ビスフェノールAのエチレンオキシド付加物およびプロピレンオキシド付加物、トリシクロデカンジオール、トリシクロデカンジメタノール、ジシクロヘキシル-4,4'-ジオールなどが挙げられる。これらのうち水素化ビス

フェノールAなどのビス(ヒドロキシシクロヘキシル)アルカンが好ましい。環式2価アルコール(C)の量は、ポリエステル樹脂を構成する全多価アルコール成分の2~60モル%であると好ましく、3~50モル%であると更に好ましい。環式2価アルコール(C)の量が少なすぎると、ガラス転移温度や溶融粘度が低くなり、耐ブロッキング性が低下したり、ホットオフセットが発生したりすることがあり、逆に脂環族2価アルコールの量が多くなりすぎると、溶融粘度が高くなり、定着性が低下することがある。

【0022】正帯電制御樹脂としてのポリエステル樹脂を構成する他のアルコール成分として、さらに鎖式2価アルコール(E)が共重縮合されていることが好ましい。また、3価以上のアルコール(G)が共重縮合されていてもよい。鎖式2価アルコール(E)としては、エチレンジグリコール、ジエチレンジグリコール、1,3-プロパンジオール、1,4-ブタンジオール、1,5-ペンタンジオール、1,6-ヘキサジオール、ジエチレンジグリコール、ポリエチレンジグリコール、ポリテトラメチレンジグリコールなどの直鎖状脂肪族グリコール；プロピレンジグリコール、ジプロピレンジグリコール、ポリプロピレンジグリコール、ネオペンチルグリコール、2,2,4-トリメチル-1,3-ペンタンジオール、2-エチル-2-プロピル-1,3-プロパンジオールなどの分岐鎖状脂肪族グリコールなどが挙げられる。これらの中でも、直鎖状脂肪族グリコールが好ましく、その中でもエチレンジグリコールが特に好ましい。鎖式2価アルコール(E)の量は、ポリエステル樹脂を構成する全多価アルコール成分の40~98モル%であると好ましく、50~97モル%であると更に好ましい。鎖式2価アルコール(E)の量が少なすぎると、溶融粘度が高くなり、定着性が低下することがあり、逆に鎖式2価アルコールの量が多くなりすぎると、ガラス転移温度や溶融粘度が低くなり、耐ブロッキング性が低下したり、ホットオフセットが発生したりすることがある。3価以上のアルコール(G)としては、トリメチロールプロパン、グリセリン、ペンタエリスリトール、ジペンタエリスリトール、トリメチロールエタン、シクロヘキサントリオール、トリス(ヒドロキシメチル)シクロヘキサンなどが挙げられる。3価以上のアルコール(G)の割合は、全アルコール成分の5モル%以下が好ましい。この割合が大きくなると、ポリエステル樹脂の重量平均分子量が高くなるために、トナーの溶融粘度が高くなり、トナーの定着性が悪くなることがある。

【0023】本発明のトナーに含有される正帯電制御樹脂としてのポリエステル樹脂の分子量は、ゲルパーミエーションクロマトグラフィー(GPC)で測定したときに、ポリスチレン換算で、数平均分子量が、1,500~20,000、好ましくは2,000~10,000であり、重量平均分子量が、好ましくは5,000~3

00, 000、好ましくは7, 000~100, 000である。分子量がこの範囲にあることによって低温定着性とホットオフセット耐性に優れたトナーを得ることができる。数平均分子量と重量平均分子量が上記範囲より小さい場合、樹脂の凝集力が低下し、保存性が悪化することがあり、逆に大きい場合、生産性が低下し、トナーの定着性が悪化することがある。また、帯電制御樹脂のガラス転移温度は、好ましくは40~90℃、特に好ましくは50~80℃である。ガラス転移温度が上記範囲であれば、トナーの保存性が改良される。

【0024】正帯電制御樹脂としてのポリエステル樹脂は、水酸基価が通常1~100mg KOH/gであり、好ましくは5~80mg KOH/gのものである。水酸基価が小さいと、定着性が悪くなり、画像の表面に大きな凹凸が生じて平滑性が低下することがある。逆に大きいと、ホットオフセット発生温度が低くなり、さらに親水性が高くなって、環境変化によって帯電量が変化しやすい傾向にある。また、帯電制御樹脂は、高温高湿環境での水分の影響を少なくするために、芳香環をより少なくすることが好ましい。

【0025】本発明のトナーに含有される正帯電制御樹脂としてのポリエステル樹脂は、公知の方法、すなわち重縮合法により製造することができる。多価カルボン酸成分と多価アルコール成分とを重縮合するにあたり、多価カルボン酸成分と多価アルコール成分とを合計した全単体中、アルコール性反応性基の水酸基価の総数

〔X〕が前記カルボン酸性反応性基の酸価の総数〔Y〕よりも小さくならない条件で行うことが、ポリエステルの分子量を高くし、且つ水酸基価を高くすることができるので好適である。アルコール性反応性基の水酸基価の総数〔X〕とカルボン酸性反応性基の酸価の総数〔Y〕との割合は〔X〕／〔Y〕の当量比1.00以上が好ましく、1.01~1.5がより好ましく、1.03~1.3の範囲が特に好ましい。ここでアルコール性反応性基とは、エステル結合を形成させるアルコール性の官能基をいい、通常、ヒドロキシル基などが挙げられる。カルボン酸性反応性基とは、エステル結合を形成させるカルボン酸性の官能基をいい、通常、カルボキシル基又はカルボン酸誘導体基などが挙げられる。

【0026】重縮合反応は、例えば、反応温度100~300℃、好ましくは150~280℃で行われ、特に不活性ガスの存在下で行うのが好ましい。必要に応じて、トルエン、キシレンなどの、水と共沸する非水溶性の有機溶媒を使用してもよい。また重縮合反応を減圧下（通常、0.1~500mmHg、好ましくは0.5~200mmHg、より好ましくは1~50mmHg）で行ってもよい。また、この重縮合反応には、通常、エステル化触媒が用いられる。エステル化触媒としては、例えば、パラトルエンスルホン酸、硫酸、リン酸などのブレンステッド酸；酢酸カルシウム、酢酸亜鉛、酢酸マン

ガン、ステアリン酸亜鉛；鉄や亜鉛のアセチルアセトナート；金属アルコキシド；アルキル錫オキサイド、ジアルキル錫オキサイド、有機チタン化合物などの有機金属化合物；酸化スズ、酸化アンチモン、酸化チタン、酸化バナジウムなどの金属酸化物；ヘテロポリ酸などが挙げられ、得られたポリエステルを高分子量化できる点でチタンアルコキシド、ヘテロポリ酸又は鉄アセチルアセトナートが好ましい。

【0027】本発明のトナーに含有される正帯電制御樹脂としてのポリエステル樹脂を得るために、上記カルボン酸化合物及びアルコールを、所望の組成比で仕込み一括して反応させてもよく、分子量の調整を行なうために次の方法を用いることもできる。即ち、環式2価カルボン酸化合物（B）と環式2価アルコール（C）とを、好ましくは、環式2価カルボン酸化合物（B）、環式2価アルコール（C）並びに鎖式2価カルボン酸化合物

（D）及び／又は鎖式2価アルコール（E）とを、重縮合させて前駆体を得、次いで、この前駆体とアミノ基若しくはその塩を含有する多価カルボン酸化合物（A1）及び／又はアミノ基若しくはその塩を含有する多価アルコール（A2）、並びに多価カルボン酸化合物（H）及び／又は多価アルコール（I）とを重縮合させる。

【0028】前駆体は、ゲルパーミエーションクロマトグラフィー（GPC）で測定したときに、ポリスチレン換算で、その数平均分子量が1,500~5,000、好ましくは、2,000~4,000である。分子量がこの範囲にあることによって樹脂の分散性が高くなる。前駆体のガラス転移温度は、好ましくは40℃以上、特に好ましくは50~80℃である。ガラス転移温度が40℃以上であればトナーの保存性が改良される。

【0029】前駆体及びアミノ基若しくはその塩を含有する多価カルボン酸化合物（A1）及び／又はアミノ基若しくはその塩を含有する多価アルコール（A2）と共重縮合させる多価カルボン酸化合物（H）は、特に制限されず、前述したような、芳香族2価カルボン酸化合物及び脂環族ジカルボン酸化合物のような環式2価カルボン酸化合物（B）、鎖式2価カルボン酸化合物（D）、3価以上のカルボン酸化合物（F）などを挙げるができる。これらの中でも、テレフタル酸、テトラヒドロテレフタル酸、ヘキサヒドロテレフタル酸のごとき、環を構成する隣り合わない2個の炭素原子それぞれにカルボキシル基又はカルボン酸誘導体基が結合した環式2価カルボン酸化合物が好ましい。前駆体及びアミノ基若しくはその塩を含有する多価カルボン酸化合物（A1）及び／又はアミノ基若しくはその塩を含有する多価アルコール（A2）と共重縮合させる多価アルコール（I）も、特に制限されず、前述したような、芳香族2価アルコールや脂環族2価アルコールのような環式2価アルコール（C）、鎖式2価アルコール（E）、3価以上のアルコール（G）などを挙げるができる。前駆体との

共重縮合に用いる、多価カルボン酸化合物(H)または多価アルコール(I)の合計量は、前駆体100重量部に対して、好ましくは10~50重量部、特に好ましくは20~40重量部である。この多価カルボン酸化合物又は多価アルコールの量が上記範囲にあることによって、溶解特性を損なわずに高分子量化することができるので好ましい。

【0030】本発明のトナーに含有される負帯電制御樹脂は、スルホン酸基若しくはその塩を含有する多価カルボン酸化合物(J1)及び/又はスルホン酸基若しくはその塩を含有する多価アルコール(J2)を重縮合してなるポリエステル樹脂からなるものである。この負帯電制御樹脂は、上述した正帯電制御樹脂を構成するアミノ基若しくはその塩を含有する多価カルボン酸化合物(A1)及び/又はアミノ基若しくはその塩を含有する多価アルコール(A2)を、スルホン酸基若しくはその塩を含有する多価カルボン酸化合物(J1)及び/又はスルホン酸基若しくはその塩を含有する多価アルコール(J2)に置き換えて重縮合することにより得ることができる。従って、共重縮合させることのできる環式2価カルボン酸化合物(B)、環式2価アルコール(C)、鎖式2価カルボン酸化合物(D)、鎖式2価アルコール(E)、3価以上のカルボン酸化合物(F)及び3価以上のアルコール(G)は、前述したものをを用いることができる。また、その製造方法も前述の方法の同様にすることができる。

【0031】負帯電制御樹脂としてのポリエステル樹脂を構成するスルホン酸基若しくはその塩を含有する多価カルボン酸化合物(J1)としては、スルホテレフタル酸、5-スルホイソフタル酸、5-スルホイソフタル酸メチルエステル、4-スルホフタル酸、4-スルホフタル酸無水物、4-スルホナフタレン-2、7-ジカルボン酸、5-[4-スルホフェノキシ]イソフタル酸；5-スルホヘキサヒドロイソフタル酸、5-スルホヘキサヒドロイソフタル酸メチルエステル、4-スルホヘキサヒドロフタル酸、4-スルホヘキサヒドロフタル酸無水物などの芳香族多価スルホン酸；5-スルホテトラヒドロイソフタル酸、5-スルホテトラヒドロイソフタル酸メチルエステル、4-スルホテトラヒドロフタル酸、4-スルホテトラヒドロフタル酸無水物などの脂環族多価スルホン酸；及びそれらの塩等が挙げられる。スルホン酸塩としては、アンモニウム、Li、Na、K、Mg、Ca、Cu、Fe等の塩が挙げられる。特に、K塩またはNa塩が好ましい。また、スルホン酸基若しくはその塩を含有する多価アルコール(J2)としては、2、3-ビス(ヒドロキシメチル)ベンゼンスルホン酸、3、5-ビス(ヒドロキシメチル)ベンゼンスルホン酸、3、4-ビス(ヒドロキシメチル)ベンゼンスルホン酸、2、5-ビス(ヒドロキシメチル)ベンゼンスルホン酸及びそれらの塩等が挙げられる。スルホン酸塩とし

ては、アンモニウム、Li、Na、K、Mg、Ca、Cu、Fe等の塩が挙げられる。特に、K塩またはNa塩が好ましい。

【0032】本発明のトナーに含有される負帯電制御樹脂としてのポリエステル樹脂において、スルホン酸基若しくはその塩を含有する多価カルボン酸化合物(J1)及び/又はスルホン酸基若しくはその塩を含有する多価アルコール(J2)の量は、ポリエステル樹脂を構成する全単量体(全カルボン酸成分と全アルコール成分との合計)の、通常、0.2~30モル%、好ましくは、0.5~10モル%である。この多価カルボン酸化合物(J1)及び/又は多価アルコール(J2)を重縮合成分として含有することによって、トナー中の顔料の分散性が向上し、トナーの帯電性を制御することができる。

【0033】ここで、本発明のトナーにおいては、正帯電制御樹脂と負帯電制御樹脂を併用するが、その割合は、トナーを正帯電性とするか、あるいは負帯電性とするかによって異なる。正帯電性トナーを得る場合には、正帯電制御樹脂中の正帯電性をもたらすアミノ基若しくはその塩のモル当量数(以下、「正官能基量」という。)を、負帯電制御樹脂中の負帯電性をもたらすスルホン酸基若しくはその塩のモル当量数(以下、「負官能基量」という。)より多くなるように、各帯電制御樹脂のトナー中の含有量を調整する。負帯電性トナーを得る場合には、負官能基量が、正官能基量より多くなるように、各帯電制御樹脂の使用割合を調整する。

【0034】具体的には、正官能基量Pは、「正帯電制御樹脂中の正帯電性をもたらすアミノ基若しくはその塩の重量%とトナー中の正帯電制御樹脂量との積を、正帯電制御樹脂中の正帯電性をもたらすアミノ基若しくはその塩を有する構造単位分子量で除したものと」して算出することができる。また、負官能基量Qは、「負帯電制御樹脂中の負帯電性をもたらすスルホン酸基若しくはその塩の重量%とトナー中の負帯電制御樹脂量との積を、負帯電制御樹脂中の負帯電性をもたらすスルホン酸基若しくはその塩を有する構造単位分子量で除したものと」して算出することができる。正帯電性トナーの場合、正官能基量Pと負官能基量Qとの比(P:Q)は、通常1:0.005~1:0.9、好ましくは1:0.01~1:0.8、より好ましくは1:0.05~1:0.7となるように各帯電制御樹脂の割合を決定する。負帯電性トナーの場合、負官能基量Qと正官能基量Pとの比(Q:P)は、通常1:0.005~1:0.9、好ましくは1:0.01~1:0.8、より好ましくは1:0.05~1:0.7となるように各帯電制御樹脂の割合を決定する。この官能基量比において、一方の比率が小さすぎると、連続印字をした場合、帯電制御能力が高くなりすぎ、印字耐久性や印字濃度が低下する、トナーが飛散するなどの不具合を生じることがある。逆に、一方の比率が大きすぎると、帯電性が不十分とな

り、カブリなどの問題を生じることがある。

【0035】本発明では、負帯電制御樹脂と正帯電制御樹脂とを併用することにより、望ましくは前記官能基比で併用することにより、低温低湿下及び高温高湿下のいずれの環境においても帯電性があまり変化せず、さらには、連続印字を行っても画質の低下やカブリの発生が抑制されるトナーを得ることができる。

【0036】本発明のトナーは、正帯電制御樹脂としてのポリエステル樹脂と負帯電制御樹脂としてのポリエステル樹脂とを、その合計で、後述の結着樹脂100重量部に対して、通常、0.01～20重量部、好ましくは0.03～10重量部含有している。ポリエステル樹脂の量が少なく帯電制御性能が頭われず、多すぎると環境変動による帯電量の变化幅が大きくなりやすい。

【0037】本発明のトナーは、上述したポリエステル樹脂以外に、他の帯電制御剤を併用しなくても実用上十分な帯電特性を示す。しかしながら微調整などの目的で、従来の帯電制御剤を併用してもよい。他の帯電制御剤として、各種の正帯電性又は負帯電性の帯電制御剤を用いることが可能である。例えば、カルボキシル基または含窒素基を有する有機化合物の金属錯体、含金属染料、ニグロシン等が挙げられる。より具体的には、スピロンブラックTRH（保土ヶ谷化学工業社製）、T-77（保土ヶ谷化学工業社製）、ポントロンS-34（オリエント化学工業社製）、ポントロンE-84（オリエント化学工業社製）、ポントロンN-01（オリエント化学工業社製）、コピーブルー-PR（クラリアント社製）等の帯電制御剤および／または4級アンモニウム（塩）基含有（メタ）アクリレート系共重合体、スルホン酸（塩）基含有アクリレート系共重合体等の他の帯電

制御樹脂を挙げることができる。

【0038】本発明トナーに含有される結着樹脂は、トナーの結着樹脂として通常に使われている重合体を使用することができる。具体的には、ポリスチレン、スチレン（メタ）アクリレート共重合樹脂、上記以外のポリエステル樹脂、ポリウレタン、エポキシ樹脂、ポリオレフィン、ポリアミド、ポリスルホン、ポリシアノアリアルエーテル、（メタ）アクリレート樹脂、ノルボルネン系樹脂、スチレン系樹脂の核水添物、スチレン-イソブレン-スチレンブロックポリマーの核水添物などが挙げ

られる。

【0039】本発明のトナーに含有される着色剤としては、黒色着色剤、イエロー着色剤、マゼンタ着色剤、シアン着色剤などがある。黒色着色剤としては、カーボンブラック、ニグロシンベースの染料類；コバルト、ニッケル、四三酸化鉄、酸化鉄マンガ、酸化鉄亜鉛、酸化鉄ニッケル等の磁性粒子；などを挙げることができる。カーボンブラックを用いる場合、一次粒径が20～40nmであるものを用いると良好な画質が得られ、またトナーの環境への安全性も高まるので好ましい。イエ

ロー着色剤としては、アゾ系顔料、縮合多環系顔料等の化合物が用いられる。具体的にはC. I. ピグメントイエロー3、12、13、14、15、17、62、65、73、83、90、93、97、120、138、155、180および181等が挙げられる。マゼンタ着色剤としては、アゾ系顔料、縮合多環系顔料等の化合物が用いられる。具体的にはC. I. ピグメントレッド48、57、58、60、63、64、68、81、83、87、88、89、90、112、114、122、123、144、146、149、163、170、184、185、187、202、206、207、209、251、C. I. ピグメントバイオレット19、等が挙げられる。シアン着色剤としては、銅フタロシアニン化合物及びその誘導体、アントラキノン化合物等が利用できる。具体的にはC. I. ピグメントブルー2、3、6、15、15:1、15:2、15:3、15:4、16、17、および60等が挙げられる。これら着色剤の量は、結着樹脂100重量部に対して、通常、0.1～50重量部、好ましくは1～20重量部である。

【0040】本発明のトナーは、低温定着性の改善、フィリング防止などの観点から離型剤を含有していてもよい。離型剤としては、例えば、低分子量ポリエチレン、低分子量ポリプロピレン、低分子量ポリブチレンなどのポリオレフィンワックス類；キャンドリラ、カルナウバ、ライス、木ロウなどの植物系天然ワックス；パラフィン、マイクロクリスタリン、ベトロラクタムなどの石油系ワックス；フィッシュアトログシュワックスなどの合成ワックス；ペンタエリスリトールテトラミステート、ペンタエリスリトールテトラバルミテート、ジベンタエリスリトールヘキサミステートなどの多官能エステル化合物などが挙げられる。これらは1種あるいは2種以上を組み合わせ使用することができる。

【0041】これらのうち、合成ワックス（特にフィッシュアトログシュワックス）、石油系ワックス、多官能エステル化合物などが好ましい。これらのなかでも示差走査熱量計により測定されるDSC曲線において、昇温時の吸熱ピーク温度が30～200℃、好ましくは50～180℃、特に好ましくは60～160℃の範囲にあるペンタエリスリトールエステルや、同吸熱ピーク温度が50～80℃の範囲にあるジベンタエリスリトールエステルなどの多官能エステル化合物が、トナーとしての定着-剥離性バランスの面で特に好ましい。とりわけ分子量が1000以上であり、スチレン100重量部に対し25℃で5重量部以上溶解し、酸価が10mg/KOH以下であるジベンタエリスリトールエステルは、定着温度低下に著効を示す。吸熱ピーク温度は、ASTM D3418-82によって測定された値である。上記離型剤の量は、結着樹脂100重量部に対して、通常、0.1～20重量部、好ましくは1～15重量部であ

る。

【0042】本発明のトナーは、体積平均粒径(d_v)が、通常、 $1\sim 10\mu m$ 、好ましくは $3\sim 8\mu m$ であり、体積平均粒径と個数平均粒径(d_p)の比(d_v/d_p)が $1\sim 2.0$ 、好ましくは $1\sim 1.5$ である。また、トナーの長径 r_l を短径 r_s で割った値(r_l/r_s)が $1\sim 1.3$ の範囲であることが好ましい。この比が大きくなると、感光体上のトナー像を紙等の転写材に転写する転写性が低下したり、画像形成装置のトナー収納部に該トナーを納めたときにトナー同士の摩擦が大きくなるので外添剤が剥離したりして、耐久性が低下することがある。

【0043】本発明のトナーは、 $120^\circ C$ での熔融粘度が、通常、 $10,000 Pa\cdot s$ 以下、好ましくは $100\sim 10,000 Pa\cdot s$ 、より好ましくは $1,000\sim 8,000 Pa\cdot s$ である。このような熔融粘度を持つトナーによれば高速での印刷によっても高画質が実現する。粘度測定は、フローテスターを用いて測定することができる。また、フローテスターによる軟化温度が、通常、 $50\sim 80^\circ C$ 、好ましくは $60\sim 70^\circ C$ であり、流出開始温度が、通常 $90\sim 150^\circ C$ 、好ましくは $100\sim 130^\circ C$ である。軟化温度が低いと保存性が低下することがあり、逆に高いと定着性が低下することがある。流出開始温度が低いとホットオフセット耐性が低下することがあり、逆に高いと定着性が低下することがある。本発明のトナーは、示差走査熱量計によるガラス転移温度が、通常、 $0\sim 80^\circ C$ 、好ましくは $40\sim 70^\circ C$ である。ガラス転移温度が低いと保存性が低下することがあり、逆に高いと定着性が低下することがある。

【0044】本発明のトナーは、テトラヒドロフラン (THF) 不溶分量が、通常、 $0\sim 50\%$ 、好ましくは $0\sim 20\%$ である。 50% 以上では、グロスの低下や透明性の悪化が発生する。THF 不溶分量は後述の方法によって測定することができる。本発明に用いる好ましいトナーは、誘電体損測定器による体積固有抵抗値($\log(\Omega\cdot cm)$)が、通常 $10\sim 13$ 、好ましくは $10.5\sim 12.5$ のものである。体積固有抵抗値が小さいと、カブリが発生することがあり、逆に大きいと、トナー飛散、カブリ、フィルミングまたはクリーニング不良が発生することがある。また、本発明のトナーは、高温高湿環境(H/H環境)、低温低湿環境(L/L環境)での帯電量変化が少ないこと、所謂環境安定性が高いことが好ましい。その際、各環境間での帯電量の変化量は $5\mu C/g$ 以下であることが好ましい。環境安定性が低い場合、カブリが発生することがある。

【0045】本発明のトナーは、加熱熔融して膜厚 $20\mu m$ にしたトナーの面積 $100\mu m\times 100\mu m$ 中に観察される長径 $0.2\mu m$ 以上の着色剤粒子数が、 50 個以下であると好ましく、 30 個以下であるとより好ましく、 20 個以下であると更に好ましい。この数が多いと

カラー画像の鮮明な色調の再現に必要な透明性等の分光特性に悪くなり、カブリが多くなり、印字濃度が低くなることがある。分光特性は、市販のプリンターでベタの印字を行い、その色調を分光色差計で測定することができる。

【0046】また、本発明のトナーは、上述したトナーの外部を他の重合体により被覆することでコアシェル構造(カプセル構造ともいう)の粒子とすることができる。コアシェル構造粒子では、内部(コア層)の低軟化点物質をそれより高い軟化点を有する物質で内包化することにより、定着温度の低温化と保存時の凝集防止とのバランスを取ることができるので好ましい。

【0047】コアシェル型トナーの場合、コア層を構成する重合体のガラス転移温度は、通常 $0\sim 80^\circ C$ 、好ましくは $40\sim 60^\circ C$ である。ガラス転移温度が高すぎると定着温度が高くなることがあり、逆に低すぎると、保存性が低下することがある。また、シェル層を構成する重合体のガラス転移温度は、結着樹脂としてコア層を構成する重合体のガラス転移温度よりも高くなるように設定する必要がある。シェル層を構成する重合体のガラス転移温度は、トナーの保存性を向上させるために、通常 $50\sim 130^\circ C$ 、好ましくは $60\sim 120^\circ C$ 、より好ましくは $80\sim 110^\circ C$ である。これより低いと保存性が低下することがあり、逆に高いと定着性が低下することがある。コア層を構成する重合体のガラス転移温度とシェル層を構成する重合体のガラス転移温度の差は、通常 $10^\circ C$ 以上、好ましくは $20^\circ C$ 以上、より好ましくは $30^\circ C$ 以上である。この差より小さいと保存性と定着性のバランスが低下することがある。

【0048】コアシェル型トナーのコア層とシェル層との重量比率は特に限定されないが、通常 $80/20\sim 99.9/0.1$ で使用ある。シェル層の割合が上記割合より小さいと保存性が悪くなり、逆に、上記割合より大きいと低温で定着し難くなることがある。

【0049】さらにトナー中の残留金属(イオン)量を制限するのが望ましい。特にマグネシウムやカルシウムなどの金属(イオン)が現像剤中に残留していると、高湿条件下では吸湿を起こし現像剤の流動性を低下させ、画質に悪影響を及ぼすことがある。マグネシウムやカルシウム(以下、単に残留金属という)の現像剤中の含有量の少ないものは、高温高湿条件下でも、1分間に30枚以上を印刷できる高速機で高い印字濃度、カブリのない良好な画質を与えることができる。残留金属量は、好ましくは $170 ppm$ 以下、より好ましくは $150 ppm$ 以下、特に好ましくは $120 ppm$ 以下である。残留金属を低減させるには、例えばトナー製造工程の脱水段階で、連続式ベルトフィルターやサイホンピーラー型セントリフュージなどの洗浄脱水機などを用いて脱水、洗浄を繰り返し行い、乾燥すればよい。

【0050】本発明のトナーは、例えば、①結着樹脂成

分となる熱可塑性樹脂中に、着色剤、正帯電制御樹脂、負帯電制御樹脂及び離型剤等を溶融混合して均一に分散させて組成物とした後、該組成物を粉碎、分級することによりトナーを得る粉碎法、②結着樹脂原料である重合性単量体中に着色剤、正帯電制御樹脂、負帯電制御樹脂及び離型剤等を溶解あるいは分散させ、重合開始剤を添加後、分散安定剤を含有する水系分散媒体中に分散させ、所定温度まで加温して重合を開始し、重合終了後に濾過、洗浄、脱水、乾燥することによりトナーを得る重合法、③乳化重合や分散重合等により得た結着樹脂の粒子と、着色剤、正帯電制御樹脂及び負帯電制御樹脂を含有してなる粒子とを、会合させた粒子を、濾過、乾燥することによりトナーを得る会合法、④親水性基含有樹脂を結着樹脂とし、それに着色剤、正帯電制御樹脂及び負帯電制御樹脂等を添加して有機溶媒に溶解させた後、該樹脂を中和して転相、その後乾燥することによりトナーを得る転相乳化法等により製造することができる。この中でも、ドット再現性の良好な画質を与えるトナーを得る観点から、重合法により得られたトナーが好ましい。

【0051】本発明のトナーの製造方法は、前述したアミノ基若しくはその塩を含有する多価カルボン酸化合物（A1）及び／又はアミノ基若しくはその塩を含有する多価アルコール（A2）を重縮合してなるポリエステル樹脂からなる正帯電制御樹脂100重量部と、着色剤10～200重量部と、該帯電制御樹脂を溶解し得る有機溶剤0～100重量部とを混合して、正帯電制御樹脂組成物を得る工程、前述したスルホン酸基若しくはその塩を含有する多価カルボン酸化合物（A1）及び／又はスルホン酸基若しくはその塩を含有する多価アルコール（A2）を重縮合してなるポリエステル樹脂からなる負帯電制御樹脂100重量部と、着色剤10～200重量部と、該帯電制御樹脂を溶解し得る有機溶剤0～100重量部とを混合して、負帯電制御樹脂組成物を得る工程とを有する。本発明のトナーの製造方法においては、正または負帯電制御樹脂100重量部と、着色剤20～150重量部を混合して得られる帯電制御樹脂組成物を用いるのが好ましい。帯電制御樹脂組成物を用いてトナーを製造することで、トナー中に着色剤を均一に分散することができる。

【0052】本発明で用いられる正または負帯電制御樹脂組成物の製造にあたり、有機溶剤を用いると、帯電制御樹脂を溶解又は膨潤させて樹脂が柔らかい状態で混合することができ、着色剤を均一に分散できるので好ましい。有機溶剤を用いない場合は、樹脂が柔らかくなる程度の温度まで加温して混合しないする必要があり、温度の制御が難しくなることがある。また、有機溶剤を用いる場合、特に有機溶剤の沸点が低いと、加温により有機溶剤が蒸発することがあるので、室温で、あるいは冷却して正または負帯電制御樹脂組成物を得ることが好ましい。尚、トナー中に有機溶剤が残存していると臭気の間

題が発生することがあるので、有機溶剤は、正または負帯電制御樹脂組成物の製造時又はトナーの製造時のいずれかで除去されることが好ましい。有機溶剤の量は、正または負帯電制御樹脂100重量部に対して0～100重量部、好ましくは5～80重量部、さらに好ましくは10～60重量部であり、この範囲にあると分散性と加工性のバランスが優れている。また、この時、有機溶剤は、一度に全量を添加しても、あるいは混練状態を確認しながら、何回かに分割して添加しても良い。

【0053】有機溶剤を用いる場合は、その溶解度係数（以下、SP値という。）が8～15 [cal/cm^3]^{1/2}であり、沸点が50～150℃の範囲のものが好ましい。SP値が8 [cal/cm^3]^{1/2}より小さいと極性が小さくなって帯電制御樹脂を溶解させることができないことがあり、また逆にSP値が15 [cal/cm^3]^{1/2}より大きいと極性が高くなって帯電制御樹脂を溶解させることができないことがある。一方、沸点が50℃より低いと混練により発生する熱で有機溶剤が蒸発することがあり、逆に150℃より高いと混練後、有機溶剤を除去することが困難になることがある。有機溶剤としては、具体的に（SP値／沸点）、メタノール（14.5／65℃）、エタノール（10.0／78.3℃）、プロパノール（11.9／97.2℃）、ジエチルケトン（8.8／102℃）、ジ-n-プロピルケトン（8.0／144℃）、ジ-i-so-プロピルケトン（8.0／124℃）、メチル-n-プロピルケトン（8.3／102℃）、メチル-i-so-プロピルケトン（8.5／95℃）、メチル-n-ブチルケトン（8.5／127℃）、メチル-i-so-ブチルケトン（8.4／117℃）、トルエン（8.9／110℃）、テトラヒドロフラン（9.1／65℃）、メチルエチルケトン（9.3／80℃）、アセトン（9.9／56℃）、シクロヘキサノン（9.9／156℃）などが挙げられ、これらは単独で用いても、2種以上を混合して用いても良い。この中でも帯電制御樹脂への溶解性、混練後の除去を考慮して、ジエチルケトン、メチル-n-プロピルケトン、メチル-n-ブチルケトン、トルエン／メタノール混合溶媒、トルエン／エタノール混合溶媒、トルエン／プロパノール混合溶媒、メチルエチルケトン／メタノール混合溶媒が好ましい。

【0054】混合は、ロール、プラスチックダー（ブラベンダー社製）、ラボプラストミル（東洋精機社製）、ニーダー、一軸押出機、二軸押出機、バンバリー、ブス・コニーダー等を用いて行うことができる。有機溶剤を用いる場合は、臭気、毒性の問題が有るので、有機溶剤が漏れない密閉系の混合機が好ましい。また、混合機にはトルクメーターが設置されていることが、トルクのレベルで分散性を管理することができるので好ましい。

【0055】本発明で用いられる正または負帯電制御樹脂

脂組成物は、該組成物に有機溶剤を添加して、5%の樹脂溶液とした後、ガラス板上に、間隙が30 μ mのドクターブレードで樹脂溶液を塗布、乾燥して得られるフィルムの単位面積100 μ m \times 100 μ m中に観察される長径0.2 μ m以上の着色剤粒子数が、20個以下であると好ましく、10個以下であるとより好ましく、5個以下であると更に好ましい。この数が多いとカラー画像の鮮明な色調の再現に必要な透明性等の分光特性に悪くなり、カブリが多くなり、印字濃度が低くなることがある。分光特性は、市販のプリンターでベタの印字を行い、その色調を分光色差計で測定する。有機溶剤を添加して、5%の樹脂溶液とした後、ガラス板上に、間隙が30 μ mのドクターブレードで混合溶液を塗布、乾燥して得られるフィルムの単位面積100 μ m \times 100 μ m中に観察される長径0.2 μ m以上の着色剤粒子数が20個以下の正または負帯電制御樹脂組成物を用いることによって、加熱溶融して膜厚20 μ mにし、面積100 μ m \times 100 μ m中に観察される長径0.2 μ m以上の着色剤粒子数が50個以下であるトナーを比較的容易に得ることができる。

【0056】本発明のトナーの製造方法においては、正または負帯電制御樹脂組成物をトナー中に包含させるには、結着樹脂と該帯電制御樹脂組成物、及び必要に応じてその他の添加剤等を溶融混練した後、冷却後所望の粒径分布となるように粉碎・分級する粉碎法、適当な水系分散媒体中で、結着樹脂の原料となる重合性単量体と帯電制御樹脂組成物、及び必要に応じてその他の添加剤とを含む重合性単量体組成物を重合する重合法等が挙げられるが、ドット再現性の良好な画質を与えるトナーが得られるので重合法で製造することが好ましい。

【0057】本発明のトナーの製造方法においては、前記正帯電制御樹脂組成物0.1~20重量部と、負帯電制御樹脂組成物の0.1~20重量部と、重合性単量体100重量部とを混合して重合性単量体組成物を得、これを水系分散媒体中で重合して、トナーを製造することが好ましい。正帯電制御樹脂組成物と負帯電制御樹脂組成物の割合は、トナーを正帯電性とするか、負帯電性とするかで、前述した官能基量比となるように、適宜変更することができる。

【0058】重合方法は特に限定されず、乳化重合、懸濁重合、分散重合、ソープフリー重合のいずれでも良いが、着色剤を均一に含有させ、帯電性、転写性を向上させることができる点から、懸濁重合法が好ましく、具体的には、重合性単量体、正帯電制御樹脂組成物、負帯電制御樹脂組成物、分子量調整剤、離型剤、及び必要に応じて帯電制御剤等の添加剤を含有する重合性単量体組成物を水系媒体中で重合する。

【0059】以下、より好ましい懸濁重合によるコアシェル型トナーの製造方法について説明する。分散安定化剤を含有する水系分散媒体中で、重合性単量体（コア用

重合性単量体）、正帯電制御樹脂組成物、負帯電制御樹脂組成物及びその他の添加剤を含有する重合性単量体組成物（コア用単量体組成物）を懸濁させ、重合開始剤を用いて重合することにより、コア粒子を製造し、更に、シェルを形成するための重合性単量体（シェル用重合性単量体）と重合開始剤を添加し、重合することでカプセルトナーを得ることができる。シェルを形成する具体的な方法としては、前記コア粒子を得るために行った重合反応の反応系にシェル用重合性単量体を添加して継続的に重合する方法、または別の反応系で得たコア粒子を仕込み、これにシェル用重合性単量体を添加して段階的に重合する方法などを挙げることができる。シェル成分用単量体は反応系中に一括して添加するか、またはプランジャポンプなどのポンプを使用して連続的もしくは断続的に添加することができる。

【0060】コア用重合性単量体として、モノビニル系単量体、架橋性単量体及びマクロモノマー等を挙げることができる。この重合性単量体が重合され、結着樹脂成分となる。モノビニル系単量体としては、具体的にはスチレン、ビニルトルエン、 α -メチルスチレン等のスチレン系単量体；（メタ）アクリル酸；（メタ）アクリル酸メチル、（メタ）アクリル酸エチル、（メタ）アクリル酸プロピル、（メタ）アクリル酸ブチル、（メタ）アクリル酸2-エチルヘキシル、（メタ）アクリル酸シクロヘキシル、（メタ）アクリル酸イソボニル、（メタ）アクリル酸ジメチルアミノエチル、（メタ）アクリルアミド等の（メタ）アクリル酸の誘導体；エチレン、プロピレン、ブチレン等のモノオレフィン系単量体；等が挙げられる。モノビニル系単量体は、単独で用いても、複数の単量体を組み合わせて用いても良い。これらモノビニル系単量体のうち、スチレン系単量体単独、スチレン系単量体と（メタ）アクリル酸の誘導体との併用などが好適に用いられる。

【0061】モノビニル系単量体と共に、架橋性単量体及び重合体を用いるとホットオフセット改善に有効である。架橋性単量体は、重合可能な炭素-炭素不飽和二重結合を2以上有する単量体である。具体的には、ジビニルベンゼン、ジビニルナフタレン、およびこれらの誘導体等の芳香族ジビニル化合物；エチレングリコールジメタクリレート、ジエチレングリコールジメタクリレート等のジエチレン性不飽和カルボン酸エステル；N,N-ジビニルアニリン、ジビニルエーテル等のビニル基を2個有する化合物、ペンタエリスリトールトリアリルエーテルやトリメチロールプロパントリアクリレート等のビニル基を3個以上有する化合物等を挙げることができる。架橋性重合体は、重合体中に2個以上のビニル基を有する重合体のことであり、具体的には、分子内に2個以上の水酸基を有するポリエチレン、ポリプロピレン、ポリエステル及びポリエチレングリコール等の重合体と、アクリル酸やメタクリル酸等の不飽和カルボン酸単

量体を縮合反応することにより得られるエステルを挙げることができる。これらの架橋性単量体及び架橋性重合体は、それぞれ単独で、あるいは2種以上組み合わせて用いることができる。使用量は、モノビニル系単量体100重量部当たり、通常10重量部以下、好ましくは、0.1~2重量部である。

【0062】また、モノビニル系単量体と共に、マクロモノマーを用いると、保存性と低温定着性とのバランスが良好になるので好ましい。マクロモノマーは、分子鎖の末端にビニル重合性官能基を有するもので、数平均分子量が、通常、1,000~30,000のオリゴマーまたはポリマーである。数平均分子量が小さいものを用いると、重合体粒子の表面部分が柔らかくなり、保存性が低下するようになる。逆に数平均分子量が大きいものを用いると、マクロモノマーの溶解性が悪くなり、定着性および保存性が低下するようになる。マクロモノマー分子鎖の末端に有るビニル重合性官能基としては、アクリロイル基、メタクリロイル基などを挙げることができ、共重合のしやすさの観点からメタクリロイル基が好ましい。

【0063】マクロモノマーは、前記モノビニル系単量体を重合して得られる重合体のガラス転移温度よりも高いガラス転移温度を有するものが好ましい。本発明に用いるマクロモノマーの具体例としては、スチレン、スチレン誘導体、メタクリル酸エステル、アクリル酸エステル、アクリロニトリル、メタクリロニトリル等を単独でまたは2種以上を重合して得られる重合体、ポリシロキサン骨格を有するマクロモノマーなどを挙げることができるが、その中でも、親水性のもの、特にメタクリル酸エステルまたはアクリル酸エステルを単独でまたはこれらを組み合わせて重合して得られる重合体が好ましい。マクロモノマーを使用する場合、その量は、モノビニル系単量体100重量部に対して、通常、0.01~10重量部、好適には0.03~5重量部、さらに好適には0.05~1重量部である。マクロモノマーの量が少ないと、トナーの保存性が向上しない。マクロモノマーの量が極端に多くなると、トナーの定着性が低下するようになる。

【0064】コア用重合性単量体のなかでも、ガラス転移温度が、通常60℃以下、好ましくは40~60℃の重合体を形成しうるものがコア用単量体として好適である。ガラス転移温度が高すぎると定着温度が高くなり、逆に低すぎると、トナーの保存性が低下する。通常、コア用単量体は1種または2種以上を組み合わせて使用しても良い。

【0065】シェル用重合性単量体としては、コア粒子を構成する重合体のガラス転移温度よりも高いガラス転移温度を有する重合体を与えるものであるのが望ましい。シェル用重合性単量体を構成する単量体として、スチレン、アクリロニトリル、メチルメタクリレートなど

のガラス転移温度が80℃を超える重合体を形成する単量体をそれぞれ単独で、あるいは2種以上組み合わせて使用することができる。シェル用重合性単量体により得られる重合体のガラス転移温度は、重合トナーの保存安定性を向上させるために、通常50~130℃、好ましくは60~120℃、より好ましくは80~110℃である。これより低いと保存安定性が低下することがあり、逆に高いと定着性が低下することがある。コア用重合性単量体からなる重合体とシェル用重合性単量体からなる重合体との間のガラス転移温度の差は、通常10℃以上、好ましくは20℃以上、より好ましくは30℃以上である。この差より小さいと保存性が低下する。

【0066】重合開始剤としては、過硫酸カリウム等の過硫酸塩；4,4'-アゾビス(4-シアノ吉草酸)、2,2'-アゾビス(2-メチル-N-(2-ヒドロキシエチル)プロピオンアミド、2,2'-アゾビス(2-アミジノプロパン)ジヒドロクロライド、2,2'-アゾビス(2,4-ジメチルバレロニトリル)、2,2'-アゾビスイソブチロニトリル等のアゾ化合物；ラウロイルパーオキシド、ベンゾイルパーオキシド、t-ブチルパーオキシ-2-エチルヘキサノエート、t-ヘキシルパーオキシ-2-エチルヘキサノエート、t-ブチルパーオキシビバレート、ジ-イソプロピルパーオキシジカーボネート、1,1,3,3-テトラメチルブチルパーオキシ-2-エチルヘキサノエート、t-ブチルパーオキシイソブチレート等の過酸化物類などを例示することができる。

【0067】これらの中でも、コア用重合性単量体組成物には油溶性の重合開始剤を選択することが好ましく、シェル用重合性単量体組成物には水溶性の重合開始剤を選択することが好ましい。コア用重合開始剤は、モノビニル系単量体100重量部に対して、0.1~20重量部、好ましくは0.3~15重量部、更に好ましくは0.5~10重量部用いる。重合開始剤は、重合性単量体組成物中に予め添加することができるが、場合によっては、造粒工程終了後の懸濁液に添加することもできる。シェル用重合開始剤の量は、水系媒体基準で、通常、0.001~1重量%である。これが少ないと重合が進まず、生産性が低下し、逆に多いと分子量が低下し、保存性が悪くなる。

【0068】重合を安定に行うために、反応液に分散安定剤を添加することができる。分散安定剤としては、例えば、硫酸バリウム、硫酸カルシウムなどの硫酸塩；炭酸バリウム、炭酸カルシウム、炭酸マグネシウムなどの炭酸塩；リン酸カルシウムなどのリン酸塩；酸化アルミニウム、酸化チタン等の金属酸化物；などの金属化合物や、水酸化アルミニウム、水酸化マグネシウム、水酸化第二鉄等の金属水酸化物；ポリビニルアルコール、メチルセルロース、ゼラチン等水溶性高分子；アニオン性界面活性剤、ノニオン性界面活性剤、両性界面活性剤等を

挙げることができ、これらは、単独で用いても、2種類以上を併用しても良い。これらのうち、金属化合物、特に難水溶性の金属水酸化物のコロイドを含有する分散安定剤は、重合体粒子の粒径分布を狭くすることができ、また分散剤の洗浄後の残存量が少なく、画像を鮮明に再現できるので好ましい。

【0069】難水溶性金属水酸化物のコロイドを含有する分散安定剤は、その製法による制限はないが、水溶性多価金属化合物の水溶液のpHを7以上に調整することによって得られる難水溶性の金属水酸化物のコロイド、特に水溶性多価金属化合物と水酸化アルカリ金属塩との水相中の反応により生成する難水溶性の金属水酸化物のコロイドを用いることが好ましい。

【0070】難水溶性金属化合物のコロイドは、個数粒径分布において、小粒径側から起算した個数累計が50%である粒径D_{p50}が0.5μm以下で、90%である粒径D_{p90}が1μm以下であることが好ましい。コロイドの粒径が大きくなると重合の安定性が崩れ、またトナーの保存性が低下する。

【0071】分散安定化剤は、モノビニル系単量体100重量部に対して、通常、0.1~20重量部の割合で使用する。この割合が0.1重量部より少ないと、十分な重合安定性を得ることが困難であり、重合凝集物が生成し易くなる。逆に、20重量部を超えると、重合後のトナー粒径が細くなり過ぎ、実用的でない。

【0072】また、分子量調整剤としては、例えば、t-ブチルメルカプタン、n-ブチルメルカプタン、n-オクチルメルカプタン等のメルカプタン類；四塩化炭素、四臭化炭素等のハロゲン化炭化水素類；などを挙げることができる。これらの分子量調整剤は、重合開始前、あるいは重合途中に添加することができる。分子量調整剤は、モノビニル系単量体100重量部に対して、通常、0.01~10重量部、好ましくは0.1~5重量部の割合で用いられる。

【0073】本発明のトナーは、そのまま電子写真の現像に使用することもできるが、通常は、トナーの帯電性、流動性、保存安定性などを調整するために、トナー粒子表面に、該トナー粒子よりも小さい粒径の微粒子（以下、外添剤という。）を付着又は埋設させて使用する。外添剤としては、無機粒子と有機樹脂粒子が挙げられる。無機粒子としては、二酸化ケイ素、酸化アルミニウム、酸化チタン、酸化亜鉛、酸化錫、チタン酸バリウム、チタン酸ストロンチウムなどが挙げられる。有機樹脂粒子としては、メタクリル酸エステル重合体粒子、アクリル酸エステル重合体粒子、スチレン-メタクリル酸エステル共重合体粒子、スチレン-アクリル酸エステル共重合体粒子、ステアリン酸亜鉛、ステアリン酸カルシウム、シェルがメタクリル酸エステル共重合体でコアがスチレン重合体で形成されたコアシェル型粒子などが挙げられる。磁性一成分系現像剤の場合には、鉄、コバル

ト、ニッケル、あるいはそれらを主体とする合金、あるいはフェライト等の酸化物、を含んでも良い。これらのうち、無機酸化物粒子、特に二酸化ケイ素粒子が好適である。また、これらの微粒子表面を疎水化処理することができ、疎水化処理された二酸化ケイ素粒子が特に好適である。外添剤の量は、特に限定されないが、トナー粒子100重量部に対して、通常、0.1~6重量部である。外添剤は2種以上を組み合わせ用いても良い。外添剤を組み合わせ用いる場合には、平均粒子径の異なる無機粒子同士または無機粒子と有機樹脂粒子を組み合わせる方法が好適である。外添剤を前記トナー粒子に付着させるには、通常、外添剤とトナー粒子とをヘンシェルミキサーなどの混合器に仕込み、攪拌して行う。また、前述した水中での重合によってトナーを調整する場合には外添剤を水分散したトナー粒子の水分散体と混合攪拌した後に粉霧乾燥するなどの湿式方式を用いることもできる。

【0074】

【実施例】次に、実施例を挙げて本発明を詳細に説明するが、本発明はこれらの実施例に限定されるものではない。これらの例中の部および%は、特記がない限り重量基準である。本実施例では、以下の方法で評価した。

1. ポリエステル樹脂特性

(1) 数平均分子量及び重量平均分子量

ポリエステルの数平均分子量及び重量平均分子量は、GPC法に従って、標準ポリスチレン換算量として算出した。

(2) 水酸基価

ポリエステルの水酸基価は、「基準油脂分析試験法」（日本油化学協会）の2, 4, 9, 2-83項に記載される方法に準じて測定した。単位はmg KOH/gである。

(3) ガラス転移温度

ポリエステル樹脂のガラス転移温度(T_g)は、JIS K 7121に規定されたDSC法に準じて測定した。単位は℃である。

【0075】2. 帯電制御樹脂組成物特性

(1) 着色剤分散性1

正または負帯電制御樹脂組成物の一部を取り出した後、帯電制御樹脂を溶解するトルエンを添加して、帯電制御樹脂組成物の5%溶液にした。ガラス板上に間隙が30μmのドクターブレードで混合溶液を塗布、乾燥させ、フィルムを作製した。このシートを光学顕微鏡にて観察し、100μm平方に存在する、長径が0.2μm以上の着色剤粒子の個数を数えた。

【0076】3. トナー特性

(1) トナーの粒径

トナーの体積平均粒径(d_v)及び個数平均粒径(d_p)は、マルチサイザー（ベックマン・コールター社製）により測定した。このマルチサイザーによる測定

は、アパーチャー径：100 μ m、媒体：イソトンII、測定粒子個数：100000個の条件で行った。

(2) トナー形状

トナーの形状は走査型電子顕微鏡で写真を撮り、その写真をネクスス9000型の画像処理装置で読み込み、トナーの長径を短径で割った値(r_l/r_s)を測定した。この時のトナーの測定個数は100個で行った。

(3) 熔融粘度

フローテスター(島津製作所製、機種名「CFT-500C」)を用いて、試料量を1.0~1.3gとして、10

開始温度：35℃、昇温速度：3℃/分、予熱時間：5分、シリンダー圧力：10.0Kgf/cm²、ダイス直径：0.5mm、ダイス長さ1.0mm、剪断応力：2.451 $\times 10^5$ Pa

(4) THF不溶分量

トナーを1g精秤して、円筒ろ紙(アドバンテック社製、86Rサイズ28 \times 100mm)に入れ、それをソックスレー抽出器にかけ、THFを下部のフラスコにい

れ、6時間抽出する。抽出後、抽出溶媒を回収し、抽出溶媒中に抽出された可溶性樹脂分をエバポレータにて分離後、精秤して、以下の計算から算出した。

THF不溶分量(%) = $(T - S) / T \times 100$

T: トナーサンプル量(g)

S: 抽出樹脂分量(g)

【0077】(5) 体積固有抵抗値

トナーの体積固有抵抗値は、トナー約3gを直径5cmの錠剤成型器に入れ、約100kgの荷重を1分間かけて試験片を作製し、それを誘電体損測定器(安藤電気社製、機種名「TRS-10型」)を用い、温度30℃、周波数1kHzの条件下で測定した。

(6) 帯電量

L/L(温度10℃、湿度20%)、N/N(温度23℃、湿度50%)、H/H(温度35℃、湿度80%)環境下における帯電量を測定し、その環境変動の状況を評価した。トナーの帯電量は、正帯電性トナーについては、市販の非磁性一成分現像方式のプリンター(ブラザー工業社製、商品名「HL1670N」)、負帯電性トナーについては、市販の非磁性一成分現像方式のプリンター(沖データ社製、商品名「マイクロライン3010C」)にトナーを入れ、前記環境下で1昼夜放置後、ハーフトーンの印字パターンを5枚印字し、その後、現像ローラ上のトナーを吸引式帯電量測定装置に吸引し、帯電量と吸引量から単位重量当たりの帯電量を測定した。

(7) 着色剤分散性2

スライドガラスに適量のトナーをのせ、その上からカバーガラスを掛け、それをホットプレートにて170℃まで加熱してトナーを熔融させ、次に、カバーガラスで力を加え、トナーを押し潰した。膜厚計(アンリツ社製、

商品名：K-402B)で測定したトナーの厚みが20 μ mの部分で、光学顕微鏡にて観察し、100 μ m平方に存在する、長径が0.2 μ m以上の着色剤粒子の個数を数えた。

【0078】4. 画質評価

(1) 色調

前述したプリンターに印字用紙をセットし、現像装置にトナーを入れ、温度35℃及び湿度80%の(H/H)環境下で一昼夜放置後、5%濃度でベタ印字を行い、分光色差計(日本電色社製、機種名「SE2000」)で測定した。

(2) 印字濃度

前述したプリンターに印字用紙をセットし、現像装置にトナーを入れ、温度35℃及び湿度80%の(H/H)環境下で一昼夜放置後、5%濃度で初期から連続印字を行い、20,000枚目印字時にベタ印字を行い、黒トナーはMcBeth透過式画像濃度測定機、カラートナーはカラー反射型濃度計(X-ライト社製、機種名「404A」)を用いて、印字濃度を測定した。

(3) カブリ

前述したプリンターを用いて、温度35℃及び湿度80%の(H/H)環境下で一昼夜放置後、5%濃度で連続印字を行い、20,000枚印字後に、ベタ印字を行い、印字を途中で停止させ、現像後の感光体上にある非画像部のトナーを粘着テープ(住友スリーエム社製、スコッチメンディングテープ810-3-18)で剥ぎ取り、それを新しい印字用紙に貼り付けた。黒トナーは、その粘着テープを貼り付けた印字用紙の白色度(B)を、白色度計(日本電色社製)で測定し、同様にして、粘着テープだけを貼り付けた印字用紙の白色度(A)を測定した。その白色度(A)と白色度(B)の差 ΔY を算出して、カブリ値とした。一方、カラートナーは、黒トナーと同様にして、前述の分光色差計を用いて、白

【0079】(4) 定着温度

前述したプリンターの定着ロール部の温度を変化できるように改造して、定着ロールの温度を変化させて、5℃刻みで、それぞれの温度での現像剤の定着率を測定し、温度と定着率の関係を求める定着試験を行った。定着率は、変化させた定着ロールの温度を安定化させるため5分以上放置し、その後改造プリンターで印字用紙にベタ印字を行い、印字した用紙のベタ領域について、テープ剥離操作前後の印字濃度の比率から計算した。すなわち、テープ剥離前の画像濃度をID前、テープ剥離後の画像濃度をID後として、定着率は、次式から算出した。

定着率(%) = $(ID後 / ID前) \times 100$

ここで、テープ剥離操作とは、試験用紙の測定部分に前

述した粘着テープを貼り、一定圧力で押圧して付着させ、その後、一定速度で紙に沿った方向に粘着テープを剥離する一連の操作である。この定着試験において、定着率 80% に該当する定着ロール温度を、現像剤の定着温度とした。

(5) ホットオフセット温度

定着温度測定と同様に、定着ロール温度を変化させて、ベタ印字を行い、ホットオフセットの発生する温度を測定した。ホットオフセットが発生した時の定着ロール温度をホットオフセット温度とした。

【0080】〔ヘキサヒドロテレフタル酸ビス(β-ヒドロキシエチル)の合成〕攪拌機、温度計、還流冷却管、分水管および窒素ガス導入管を備えた三ツ口フラスコに、1, 4-シクロヘキサジカルボン酸 557 部、及びエチレングリコール 443 部を仕込んだ。窒素ガスを導入しながら攪拌を行い、反応中に生成する水を除去しながら 180℃ で 5 時間反応させた。反応温度を 200℃ に上げてフラスコ内の圧力を少しずつ減じ、1.5 時間後に 5 mmHg 以下にし、その後さらに 2 時間反応を続けて、ヘキサヒドロテレフタル酸ビス(β-ヒドロキシエチル)を得た。ヘキサヒドロテレフタル酸ビス(β-ヒドロキシエチル)は無色透明の液体であった。

【0081】〔ポリエステル樹脂の合成〕

(合成例 1) 攪拌機、温度計、還流冷却管、分水管および窒素ガス導入管を備えた三ツ口フラスコに、4-メチル-ヘキサヒドロフタル酸無水物 366 部、ヘキサヒドロテレフタル酸ビス(β-ヒドロキシエチル) 100 部、5-アミノヘキサヒドロイソフタル酸ジメチルエステル 100 部、2, 2-ビス(4-ヒドロキシシクロヘキシル)-プロパン 284 部、及びエチレングリコール 150 部を仕込んだ。水酸基価の総数〔X〕/酸価の総数〔Y〕の比は 1.19 である。窒素ガスを導入しながら攪拌を行い、反応中に生成するアルコールを除去しながら 200℃ で 3 時間反応させた。次にテトラブトキシタネート 5 部を添加し、反応温度を 220℃ に上げてフラスコ内の圧力を少しずつ減じ、1.5 時間後に 5 mmHg 以下にし、その後さらに 3 時間反応を続けて、ポリエステル樹脂(1)を得た。得られたポリエステル樹脂(1)は数平均分子量が 3,100、重量平均分子量が 10,300、水酸基価が 68 mg KOH/g、ガラス転移温度が 62℃ であった。

【0082】(合成例 2) 攪拌機、温度計、還流冷却管、分水管および窒素ガス導入管を備えた三ツ口フラスコに、4-メチル-ヘキサヒドロフタル酸無水物 366 部、ヘキサヒドロテレフタル酸ビス(β-ヒドロキシエチル) 100 部、5-ナトリウムスルホイソフタル酸ジメチルエステル 150 部、2, 2-ビス(4-ヒドロキシシクロヘキシル)-プロパン 234 部、及びエチレングリコール 150 部を仕込んだ。水酸基価の総数〔X〕/酸価の総数〔Y〕の比は 1.11 であった。窒素ガス

を導入しながら攪拌を行い、反応中に生成するアルコールを除去しながら 200℃ で 3 時間反応させた。次にテトラブトキシタネート 5 部を添加し、反応温度を 220℃ に上げてフラスコ内の圧力を少しずつ減じ、1.5 時間後に 5 mmHg 以下にし、その後さらに 3 時間反応を続けて、ポリエステル樹脂(2)を得た。得られたポリエステル樹脂(2)は数平均分子量が 3,400、重量平均分子量が 12,000、水酸基価が 52 mg KOH/g、ガラス転移温度が 63℃ であった。

10 【0083】(合成例 3) 攪拌機、温度計、還流冷却管、分水管および窒素ガス導入管を備えた三ツ口フラスコに、ヘキサヒドロフタル酸 317 部、テレフタル酸 329 部、ネオペンチルグリコール 304 部及びトリメチロールプロパン 50 部を仕込んだ。水酸基価の総数

〔X〕/酸価の総数〔Y〕の比は 1.10 である。窒素ガスを導入しながら攪拌を行い、反応中に生成するアルコールを除去しながら 200℃ で 3 時間反応させた。次に酢酸亜鉛 0.5 部を添加し、反応温度を 220℃ に上げてフラスコ内の圧力を少しずつ減じ、1.5 時間後に 5 mmHg 以下にし、その後さらに 3 時間反応を続けて、ポリエステル樹脂(3)を得た。得られたポリエステル樹脂(3)は数平均分子量が 2,900、重量平均分子量が 5,500、水酸基価が 72 mg KOH/g、ガラス転移温度が 53℃ であった。

【0084】〔正帯電制御樹脂組成物の製造〕

(参考例 1) 帯電制御樹脂として、合成例 1 で得られたポリエステル樹脂(1) 100 部に、メチルエチルケトン 24 部、メタノール 6 部を分散させ、冷却しながらロールにて混練した。帯電制御樹脂がロールに巻き付いたところで、マゼンタ顔料(クライアント社製、商品名「C. I. ピグメントバイオレット 19」) 100 重量部を徐々に添加して、1 時間混練を行い、帯電制御樹脂組成物(1-1)を製造した。この時、ロール間隙は、初期 1 mm であり、その後徐々に間隙を広げ、最後は 3 mm まで広げ、有機溶剤(メチルエチルケトン/メタノール = 4/1 混合溶剤)は、帯電制御樹脂の混練状態に合わせ何回か追加した。帯電制御樹脂組成物の一部を取り出した後、トルエンを加えて溶解させ、トルエンの帯電制御樹脂組成物の 5% 溶液にした。ガラス板上に、間隙が 30 μm のドクターブレードで混合溶液を塗布、乾燥させ、シートを作製した。このシートを光学顕微鏡にて観察したところ、100 μm 平方に存在する、長径が 0.2 μm 以上の着色剤粒子は存在しなかった。

【0085】(参考例 2~3) 着色剤としてマゼンタ顔料(クライアント社製、商品名「C. I. ピグメントバイオレット 19」)の代わりに、シアン顔料(クライアント社製、商品名「C. I. ピグメントブルー 15:3」)またはイエロー顔料(クライアント社製、商品名「C. I. ピグメントイエロー 180」)を用いた他、参考例 1 と同様にして正帯電制御樹脂組成物(1-

2及び1-3)を得た。このときの着色剤分散性1の結果を表1に示す。

【0086】[負帯電制御樹脂組成物の製造]

(参考例4~6) ポリエステル樹脂(1)の代わりに、合成例2で得られたポリエステル樹脂(2)を使用した以外は、参考例1~3と同様にして負帯電制御樹脂組成物(2-1~2-3)を得た。このときの着色剤分散性1の結果を表1に示す。

【0087】[樹脂組成物の製造]ポリエステル樹脂

(1)の代わりに、合成例3で得られたポリエステル樹脂(3)を使用した以外は、参考例1~3と同様にして樹脂組成物(3-1~3-3)を得た。このときの着色剤分散性1の結果を表1に示す。

【 0 0 8 8 】

【表 1】

顔料の種類 量 (部)	参考例								
	1	2	3	4	5	6	7	8	9
	マゼンタ 100	シアン 100	イエロー 100	マゼンタ 100	シアン 100	イエロー 100	マゼンタ 100	シアン 100	イエロー 100
ポリエステル樹脂 (1)	100	100	100		100	100			100
ポリエステル樹脂 (2)				100			100	100	
ポリエステル樹脂 (3)									
樹脂組成物	1-1	1-2	1-3	2-1	2-2	2-3	3-1	3-2	3-3
着色分散性1 (個)	0	0	0	0	0	1	74	63	94

【0089】 [トナーの製造]

(実施例 1) イオン交換水 250 部に塩化マグネシウム（水溶性多価金属塩）9.8 部を溶解した水溶液に、イオン交換水 50 部に水酸化ナトリウム（水酸化アルカリ金属）6.9 部を溶解した水溶液を攪拌下で徐々に添加して、水酸化マグネシウムコロイド（難水溶性の金属水酸化物コロイド）分散液を調製した。生成した前記コロイドの粒径分布を液滴の個数平均粒径 D50（個数粒径分布の 50% 累積値）と D90（個数粒径分布の 90% 累積値）は、粒度分布測定装置（島津製作所株式会社製、機種名「SALD2000A 型」）により測定した。この粒径分布測定器による測定においては、屈折率 = 1.55 - 0.20i、超音波照射時間 = 5 分間、液滴測定時の分散媒として 10% 食塩水使用の条件で行った。スチレン 80.5 部、アクリル酸ブチル 19.5 部、ジビニルベンゼン 0.5 部及びポリメタクリル酸エステルマクロモノマー（東亜合成化学工業社製、商品名「AA6」、Tg = 94℃）0.3 部からなるコア用重合性単量体と、上述した正帯電制御樹脂組成物（1 - 1）11 部、負帯電制御樹脂組成物（2 - 1）1 部、トードシルメルカプタン 2 部及びジベンタエリスリトールヘキサミリスレート 10 部とをメディア型湿式粉碎機を用いて湿式粉碎を行い、コア用重合性単量体組成物を得た。一方、メタクリル酸メチル 2 部と水 100 部を超音波乳化機にて微分散化処理して、シェル用重合性単量体の水分散液を得た。シェル用重合性単量体の液滴の粒径は、前記粒度分布測定装置で測定したところ、Dp90 が 1.6 μm であった。

【0090】前記により得られた水酸化マグネシウムコロイド分散液に、前記コア用単量体組成物を投入し、液滴が安定するまで攪拌し、そこに α -ブチルパーオキシ-2-エチルヘキサノエート（日本油脂社製、商品名「パーブチルO」）5部を添加後、エバラマイルダー（荏原製作所社製、機種名「MDN303V」）を用いて、15,000rpmの回転数で30分間高剪断攪拌して、単量体組成物の液滴を造粒した。この造粒したコア用重合性単量体組成物の水分散液を、攪拌翼を装着した反応器に入れ、90℃で重合反応を開始させ、重合転化率がほぼ100%に達したときに、サンプリングし、コアの粒径を測定した。この結果、体積平均粒径（ d_v ）は7.3 μ mであった。更に、前記シェル用重合性単量体の水分散液、及び2,2'-アゾビス（2-メチル-N-（2-ヒドロキシエチル）-プロピオンアミド（和光純薬社製、商品名「VA-086」）0.2部を、蒸留水65部に溶解した水溶液を反応器に入れた。8時間重合を継続した後、反応を停止し、pH9.5のトナー粒子の水分散液を得た。

【0091】前記により得たトナー粒子の水分散液を攪拌しながら、硫酸により系のpHを5以下にして酸洗浄（25℃、10分間）を行い、濾過により水を分離した
50 後、新たにイオン交換水500部を加えて再スラリー化

し水洗浄を行った。その後、再度、脱水と水洗浄を数回繰り返して、固形分を濾過分離した後、乾燥機にて45℃で2昼夜乾燥を行い、トナー粒子を得た。乾燥したトナー粒子を取り出し、測定した体積平均粒径(d_v)は7.3 μm であり、体積平均粒径(d_v)/個数平均粒径(d_p)は1.21であった。 r_l/r_s は1.1、ゲル量は15%であった。また、単位面積中に存在する、長径が0.2 μm 以上の着色剤粒子の数はなかった。前記により得られたトナー粒子100部に、疎水化処理されたコロイダルシリカ(クラリアント社製、商品名「HDK2150」)0.6部を添加し、ヘンシェルミキサーを用いて混合して正帯電性トナーを調製した。得られたトナーの特性及び画像等の評価を表2に示す。

【0092】(実施例2～3)実施例1において、使用する正帯電制御樹脂組成物と負帯電制御樹脂組成物の量を表2のように変更した他は実施例1と同様にして、正*

【表2】

	実施例			比較例		
	1	2	3	1	2	3
顔料の種類	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー
正帯電樹脂組成物 (1-1)	11					
(1-2)		10.5				
(1-3)			10			
負帯電樹脂組成物 (2-1)	1					
(2-2)		1.5				
(2-3)			2			
樹脂組成物 (3-1)				12		
(3-2)					12	
(3-3)						12
正帯電制御剤				1	1.5	2
トナー特性						
d_v (μm)	7.3	7.1	7.2	7.4	7.2	7.5
d_v/d_p	1.21	1.22	1.21	1.25	1.25	1.28
形状 (r_l/r_s)	1.1	1.2	1.1	1.2	1.2	1.3
熔融粘度 ($\text{Pa}\cdot\text{s}$)	7400	8100	6900	8500	8600	7900
THF不溶分量 (%)	15	20	18	35	27	36
体積固有抵抗 ($\log(\Omega\cdot\text{cm})$)	11.4	11.7	11.5	11.6	11.3	11.5
官能基量比 (P:Q)	1:0.09	1:0.15	1:0.21	—	—	—
L/L帯電 ($\mu\text{C/g}$)	24	26	26	45	38	56
N/N帯電 ($\mu\text{C/g}$)	24	25	24	24	25	24
H/H帯電 ($\mu\text{C/g}$)	23	23	22	10	7	22
着色剤分散性2 (個)	0	1	1	85	71	65
画質評価						
色調 L *	62.2	69.3	95.8	71.6	76.7	95.9
a *	76.9	-19.3	-18.2	51.5	-18.2	-16.8
b *	-28.3	-40.4	83.9	-21.2	-29.3	65.8
印字温度	1.45	1.48	1.47	1.35	1.38	1.39
カブリ	0.3	0.3	0.7	8.7	14.1	3.6
定着温度 (°C)	130	130	125	145	140	145
オフセット発生温度 (°C)	220	220	220	220	220	220

【0095】(実施例4～6)実施例1において、使用する正帯電制御樹脂組成物と負帯電制御樹脂組成物の量を表2のように変更した他は実施例1と同様にして、負帯電性トナーを得た。得られたトナーの特性及び画像の評価結果を表3に示す。

【0096】(比較例4～6)実施例1において、正帯電制御樹脂組成物及び負帯電制御樹脂組成物を使用する代わりに、参考例7で得られた樹脂組成物(3-1)と帯電制御剤としてサリチル酸金属塩帯電制御剤(オリエント化学工業社製、商品名「ボントロンE-84」)と

* 帯電性トナーを得た。得られたトナーの特性及び画像の評価結果を表2に示す。

【0093】(比較例1～3)実施例1において、正帯電制御樹脂組成物及び負帯電制御樹脂組成物を使用する代わりに、参考例7で得られた樹脂組成物(3-1)と帯電制御剤として第4級アンモニウム塩帯電制御剤(オリエント化学工業社製、商品名「ボントロンP-51」)とを表2の処方で使用してコア用重合性単量体組成物を作製した他は、実施例1と同様にして正帯電性トナーを得た。得られたトナーの特性及び画像等の評価を表2に示す。ここで、比較例1～3の正帯電性トナーは、着色剤の種類が同じである実施例1～3の正帯電性トナーと、温度23℃、湿度50%で測定する帯電量が同じになるように正帯電制御剤量を制御して製造した。

【0094】

【表2】

を表3の処方で使用してコア用重合性単量体組成物を作製した他は、実施例1と同様にして負帯電性トナーを得た。得られたトナーの特性及び画像等の評価を表3に示す。ここで、比較例4～6の負帯電性トナーは、着色剤の種類が同じである実施例4～6の負帯電性トナーと、温度23℃、湿度50%で測定する帯電量が同じになるように負帯電制御剤量を制御して製造した。

【0097】

【表3】

【表 3】

	実施例			比較例		
	4	5	6	4	5	6
顔料の種類	マゼンタ	シアン	イエロー	マゼンタ	シアン	イエロー
正帯電樹脂組成物 (1-1)	2					
(1-2)		1.5				
(1-3)			1			
負帯電樹脂組成物 (2-1)	10					
(2-2)		10.5				
(2-3)			11			
樹脂組成物 (3-1)				12		
(3-2)					12	
(3-3)						12
負帯電制御剤				2	1.5	0.8
トナー特性						
d _v (μm)	7.1	7.0	7.1	7.2	7.1	7.3
d _v /d _p	1.22	1.21	1.21	1.27	1.24	1.30
形状 (r ₁ /r _s)	1.1	1.2	1.1	1.2	1.2	1.3
熔融粘度 (Pa·s)	7500	7400	6800	9200	8400	7700
THF不溶分量 (%)	21	19	23	38	28	31
体積固有抵抗 (log (Ω·cm))	11.5	11.6	11.7	11.7	11.3	11.6
官能基量比 (P:Q)	0.21:1	0.13:1	0.09:1	—	—	—
L/L帯電 (μC/g)	-23	-23	-24	-40	-28	-66
N/N帯電 (μC/g)	-22	-22	-23	-22	-22	-23
H/H帯電 (μC/g)	-21	-20	-21	-18	-19	-20
着色剤分散性 2 (個)	2	0	1	96	69	78
画質評価						
色調 L*	56.9	75.5	87.3	67.2	81.4	87.8
a*	78.1	-30.2	-17.9	47.4	-22.5	-13.3
b*	-34.4	-30.4	77.6	-23.3	-20.3	48.2
印字濃度	1.55	1.54	1.49	1.37	1.37	1.38
カブリ	0.1	0.3	0.5	4.2	5.6	3.3
定着温度 (°C)	130	135	130	145	145	140
オフセット発生温度 (°C)	220	220	220	220	220	220

【0098】表2及び3より、正帯電制御樹脂としてアミノ基若しくはその塩を含有する多価カルボン酸化合物 (A1) 及び／又はアミノ基若しくはその塩を含有する多価アルコール (A2) を重縮合してなるポリエステル樹脂及び負帯電制御樹脂としてスルホン酸基若しくはその塩を含有する多価カルボン酸化合物 (J1) 及び／又はスルホン酸基若しくはその塩を含有する多価アルコール (J2) を重縮合してなるポリエステル樹脂含有しない比較例1～6のトナーは、帯電量を顔料分散性と色調が悪く、印字濃度も低く、カブリが多いことがわかる。これに対して、本発明のトナーは、環境安定性が高く、顔料分散性や色調が良好で、印字濃度が高く、カブリも

少なくできることが分かる。

【0099】

【発明の効果】本発明のトナーは、省電力、クイックスタートが可能な耐熱フィルムとサーマルヘッドを組み合わせた定着機器においても、定着開始温度とオフセット開始温度との間隔が広く、良好な低温定着特性と、高い定着画像の表面平滑性と、高温保存性を示す。また、帯電量の安定性に優れ、着色剤の分散性に優れるので、カラー画像の再現性が高く、鮮明な画像を得ることができ、カブリが少なく、印字濃度も高くすることができ、更に耐久印字性にも優れている。